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Watershed Sensitivity Measurement Strategy for Identifying Resources at Risk from Acidic Deposition

Institute of Ecology, Indianapolis, IN

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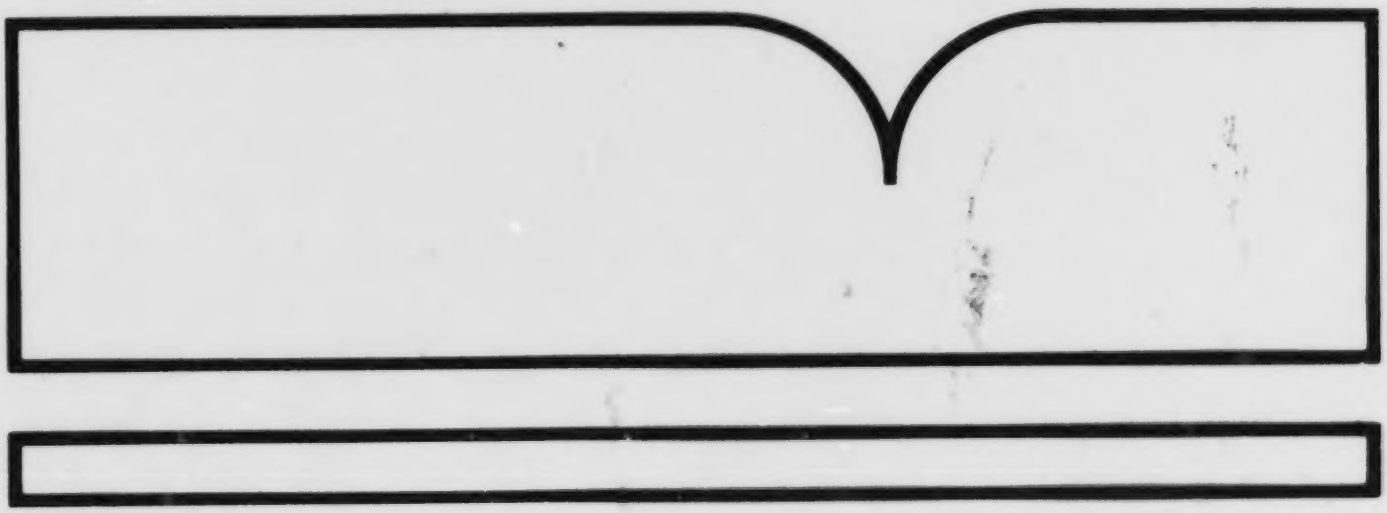

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WATERSHED SENSITIVITY MEASUREMENT STRATEGY FOR IDENTIFYING RESOURCES AT RISK FROM ACIDIC DEPOSITION

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16. ABSTRACT

Several lines of research on the effects of acidic deposition have been supported by EPA through its Environmental Research Laboratories and through a Cooperative Agreement with North Carolina State University. The study reported here was carried out as a subcontract to The Institute of Ecology from N.C. State University for research supporting programs at the Environmental Research Laboratory-Duluth. The objectives included review of existing literature on the use of indices for quantifying resource status and predicting long-term trends in relation to acidic deposition, review of options as to the form of a "sensitivity index" or loading tolerance model for use in determining resources at risk, and identification of validation steps needed to complete testing of the measure or model, and to begin its application.

One section of the report describes the suite of measures which, when taken together, best identify areas potentially sensitive to acidic inputs. Each of the component measures, when viewed separately, has certain limitations which prevent it from being an adequate measure of sensitivity; when considered together, however, as an integrative measure, the limitations are less significant.

For non-agricultural systems, forest site index appears to be a well-established integrative measure capable of responding to altered soil and water chemistry. The extent to which site index is related to changes in cation nutrient storage (due to cation stripping by acid precipitation) or other pollutant impacts still is incompletely documented, however. Measurements of aquatic sensitivity have been developed more fully, and a number of experimental and field data-based approaches exist. These include the Calcite Saturation Index, the Henrickson nomograph, the Almer/Dickson relation and an additional measure proposed here based on pH shock effects during acid flushing events. This integrative response property appears to describe a complex environment leading to species and population effects associated with periodic but physiologically important exposures to H^+ and Al^{3+}.

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SECTION I

INTRODUCTION

Orie L. Loucks, David Rapport, and Richard Miller

Atmospheric deposition of acidic pollutants appears to have increased in both area and intensity since the middle 1950's (Likens et al. 1979) and possibly over a longer time (Davis 1980). This increase has been correlated with increasing use of fossil fuel for automobiles as well as electricity, and the associated releases of oxides of nitrogen and sulfur to the atmosphere. Utility emissions increased most rapidly during the 1960's (EPA 1978), and, increasingly over this period, were emitted from elevated stack heights where dispersion in the lower atmosphere (rather than local scavenging) becomes more effective. Once in the atmosphere, the emissions can be converted to nitric and sulfuric acids. Processes of rainfall and dry deposition then lead to the accumulation of these products once again on land and surface water resources. Despite questions as to rates of reactions and the control mechanisms, enough is known about the acidic deposition phenomenon, however, to describe the principal types of impact, the mechanisms by which effects are expressed, and the nature and variability in resource response times.

Figure I-1 is a conceptual model showing reactions, transport pathways and the principal ecological consequences resulting from atmospheric deposition of elevated ozone, hydrogen, nitrate and sulfate ions. The materials and processes producing the ultimate effects of this deposition must be viewed as a coupled system which, for simplicity, is shown here as a flow diagram. The effects of interest are the direct effects on vegetation, the alteration of groundwater and associated stream chemistry, the alteration of soil chemistry and associated terrestrial productivity, and the effects on fish and other biota in aquatic systems. These effects are largely mediated through the watershed, although direct flux of acidic materials to surface waters can be important in some situations. The magnitude of the effects will vary depending on characteristics of the watershed; only those ecosystems with little or no carbonate buffering are likely to show the listed effects from acidic inputs. The actual mechanisms of the chemical and biological transformations implied in Figure I-1 are complex and will be discussed throughout the report.

Effects from oxidants and acid precipitation are both partly transient and partly irreversible in nature. Transient effects include alteration of soil solution chemistry and adverse impacts on crops, forests, fish and other biota. Irreversible effects include long-term changes in species composition, stripping of cation nutrients from soil systems, modification of groundwater, and relatively permanent reduction of buffering capacity for entire catchment areas (see later sections for references). Nutrients leached from the soil column are permanently lost, and because of the rates of natural leaching, geological replacement may be on the order of thousands of years. Shallow groundwater can be described as a sink for sulfate and hydrogen ions, heavy metals and aluminum leached from the soil column, but these ions also reach surface waters.

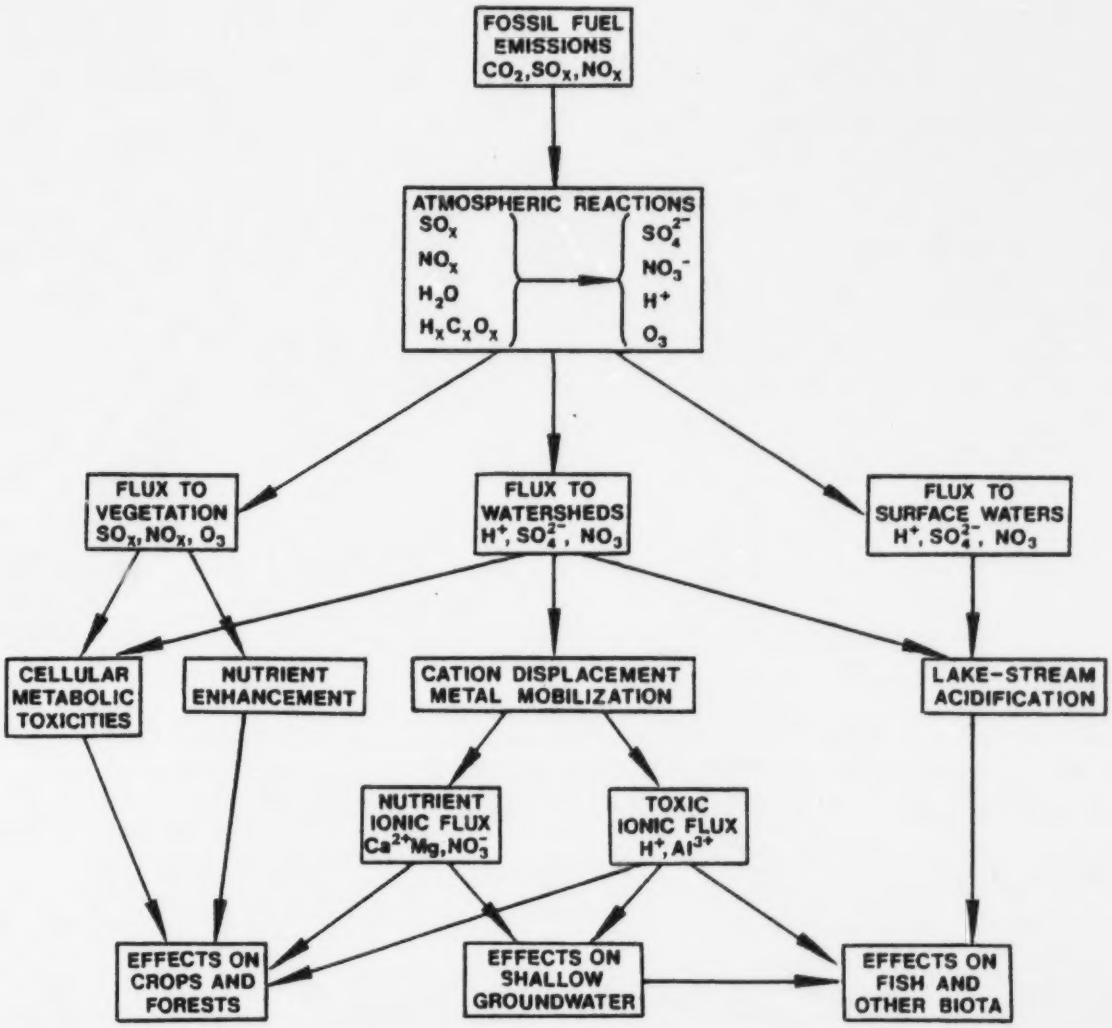

Figure I-1. Flow diagram showing system linkages for acid precipitation formation, deposition and effects as a consequence of nitrogen and sulfur oxide emissions from fossil fuel combustion.

Once in the groundwater system, these elements can influence drinking water. Acid-altered groundwater is released slowly as seepage to springs and other surface waters.

Government, industry, and the public are all concerned with the long-term responses to deposition of ozone and acidic pollutants. One possible response is the control of atmospheric inputs through reductions of SO_2 and NO_x emissions from fossil fuel combustion, a responsibility of regulatory agencies at state and federal levels of government. Glass et al. (1980) reported on a series of workshops held in late 1979 with state regulatory personnel of Wisconsin, Minnesota and Michigan regarding their concerns with and role in emissions control and environmental protection. These three states contain large areas characteristic of the sensitive resources being affected elsewhere, although acidification responses in lakes have not yet been demonstrated.

There was considerable interest among the 1979 workshop participants in controlling the precursors of acid deposition, while recognizing that there must be a clear indication of the prospective benefits in resource protection to be gained from such action. This interest resulted in specific suggestions for development of a "damage susceptibility index" which could be used to inventory susceptible resources in regions that are not yet seriously affected. Specific criteria suggested for such an index included (1) identification of buffering capacity of the lake/watershed system, and (2) consideration of potential effects on all biological resources, including timber and fish.

CONCEPTS OF MEASUREMENT FOR ECOSYSTEM RESPONSES TO ACID DEPOSITION

The loading rate of pollutants that is just below a rate producing demonstrable effects can be defined as a loading tolerance for a system with a defined sensitivity. This tolerance and sensitivity must be related to specific effects observed and to measurable lake/ watershed characteristics - chemical, geological, and biological. The pathways by which effects of acidification are expressed in ecosystems are indicated in Figure I-1 as sequential events: Fossil fuel emissions, followed by atmospheric reactions, deposition, chemical changes and, finally, biological effects. While this sequence is an oversimplification, given the state of existing knowledge, one could expect that early symptoms of acidification need not lie solely in altered biota, nor in the chemical properties of the soils and water. Various biological measures might be responsive solely to the periodic onset of acid stress. For example, changes in the establishment and recovery patterns of algal species at the mouth of a stream receiving acidic pulses from spring snowmelt could be a very sensitive measure of irregularly expressed stresses.

In developing indicators of pollutant impacts on both terrestrial and aquatic ecosystems, three classes of measures can be used to reflect system transformations (Rapport and Regier 1980). Two of these, termed here "indicators" and "integrators," are well suited to representing the effects of acidification. The third, the so-called "environmental quality index," is basically unsound because it attempts to compress the many dimensions of environmental transformation into a single dimensionless

index number, often without benefit of a scientifically valid model or logical basis for such a representation. It appears to be unwise to attempt construction of environmental quality indices, or agglomerative measures of environmental quality to reflect environmental transformation, whether due to acid rain or any other factors. Inhaber (1974) proposed such an index for Canada, and the results have led to a general disenchantment with the environmental index approach.

The alternative, namely to suggest a suite of direct or relatively direct measures which reflect various dimensions of the impact process, and which are based on scientifically sound models, appears more promising (Rapport and Regier 1980). These two types of measures can be defined as follows:

> Indicators - measures of ecosystem alteration which are relatively specific or diagnostic of particular types of stresses, and which are likely to be useful as early warning of stressed environments. Some examples in the acid rain context include reduction in the populations of short-lived sensitive species and specific chemical changes such as the mobilization of aluminum during acid flushing events. Indicators must be suited to picking up transient events which may otherwise be difficult to measure.
>
> Integrators - measures of ecosystem alteration which are capable of reflecting a number of stress impacts through time, and which reflect these impacts retrospectively and synergistically. An example is the forest site index measure which integrates a variety of environmental transformations as they affect forest responses (growth and productivity) over the lifespan of the trees being measured.

To a large extent these two types of measures complement each other. The "indicators" are diagnostic of particular types of stresses, and would, due to their greater specificity, function in evaluating both causative and curative strategies. On the other hand, the integrators, although retrospective and often non-specific, overcome to a large degree the difficulty of capturing short-term events and synergistic effects in the ecosystem. To use a medical analogy, the integrators are somewhat akin to the "vital signs" of an ecosystem, while the indicators function as the clinical symptoms of distress (Rapport et al. 1980).

STUDY OBJECTIVES

The initial sections of this report have as their objective a review of the various measurements and relationships being used to quantify resource status in oxidant and acid-stressed systems, and to identify integrative measures of lake/watershed response to acidic pollutants. Considering the voluminous literature on the subject and the many possible effects, the review will be limited to those topics most closely related to the effects described in Figure I-1.

A second objective will be to examine a group of measures and/or models selected to represent ecosystem responses, such as resource nutrient cycling and biotic composition and quality. These measures require a compromise between generality, reality and precision because not all of these qualities can be achieved simultaneously (Levins 1968). The emphasis in the report will be on generality and reality for the time being. The measures used must enhance the likelihood of prediction of future lake/watershed responses in lightly impacted systems, given current acid loading rates over the period of a few decades.

Finally, the data needed to evaluate the usefulness of a group of measures or predictive models will be identified. The entire group of measures should be tested and verified with appropriate studies before effective regulatory use can be expected. The final test, application, can be met best if all others are satisfied, and if the measures relate to obvious economic benefits from acidic pollutant abatement.

SECTION II

SUMMARY AND FINDINGS

Orie L. Loucks

In August, 1979, President Jimmy Carter established a ten-year federally funded acid rain assessment program. At about the same time, the Environmental Protection Agency awarded a Cooperative Agreement to North Carolina State University to conduct a program of subcontracted studies on biological effects of acid precipitation. The Institute of Ecology (TIE) was awarded a subcontract entitled "Assessment of the Sensitivity Index Concept for Evaluating Resources at Risk from Atmospheric Pollutant Deposition (Acid Rain)," to be carried out in support of studies at the ERL-Duluth, U.S. Environmental Protection Agency.

The study was concerned principally with developing sensitivity measures for evaluating terrestrial and aquatic resources at risk from atmospheric pollutant deposition (oxidants as well as acid rain). The main objectives have been:

(1) To review existing literature on the use of indices for quantifying resource status, predicting long-term trends in ecosystem and resource responses to acid deposition, and for assessing overall risks from atmospheric pollutant deposition in relation to air emissions management;

(2) To consider several options as to the form of a "sensitivity index" or pollutant loading tolerance model for use in determining resources at risk from energy development, and outline how such a measure would function in regional inventory of risk from pollutant deposition or in the assessment of benefit from acid precursor control;

(3) To identify validation steps needed, data required (existing data or new measurements), and the steps required to complete testing and begin application of the sensitivity measures or loading tolerance model in regional and national energy development decisions.

APPROACH

Early in the study, attempts were made to compress various acid rain indices (i.e., the McFee soil sensitivity measure, the Calcite Saturation Index, etc.) into one sensitivity index. As this concept was examined, it was recognized as an unsound approach because it attempts to express too many dimensions of environmental transformation into a single dimensionless index number. Instead, a suite of integrative sensitivity measures was considered which, when viewed as a whole, would be more likely to be suitable for quantifying sensitive systems and their response to pollutant inputs. To provide a technical basis for considering such measures, an

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extensive review is presented on the mechanisms by which pollutant inputs alter the biological productivity of terrestrial and aquatic systems.

RESULTS

One major section of the report, entitled Sub-Components of Lake/Watershed Sensitivity, contains the background material on pertinent characteristics of acid precipitation effects on soils, lakes and watersheds, and lays a foundation for both the recommended sensitivity measures and the outline of research and data needs in later sections. This section also provides an understanding of the various processes occurring within the system, information that is required for developing and evaluating measures of watershed/lake sensitivity. Topics of interest include hydrologic flows, the nitrogen and sulfur cycles, alkalinity relationships, interactions of acids with organic material, nutrient stripping, H^+ toxicity, the mobilization and toxicity of aluminum and heavy metals, and synergisms between H^+, aluminum and heavy metals.

The section principally focused on new results, entitled Methodologies for Identifying Sensitive Terrestrial and Aquatic Areas, describes the various options for measures that best identify potentially sensitive areas. Three separate measures are employed for the terrestrial component: McFee's (1980) soil sensitivity classification based on cation exchange capacity; the soil sensitivity classification based on base saturation (Coote et al. 1980); and the forest site index. The site index (SI) concept has been accepted as a measure of forest productivity for many decades and is examined here as a methodology for measuring changes in potential forest growth due to long-term acidic inputs. The magnitude of site index changes due to a combination of oxidants, changes in cation nutrient storage (resulting from cation stripping by acidic precipitation), and aluminum toxicity effects is still incompletely quantified, however. Studies will be required using available data bases on oxidant exposures, apparent changes in total nutrient stocks, and aluminum mobilization in relation to acidic inputs.

Integrative measures for expressing aquatic sensitivity have been developed more fully, and a number of experimental and field data-based methods exist. These include the Calcite Saturation Index, the Henricksen nomograph and the Almer/Dickson relation. An additional measure, based on pH shock effects during acid flushing events, attempts to identify species/population impacts associated with short-term, physiologically important exposures of critical life stages to H^+ and Al^{3+}. This approach can be quantified for the pH depression levels already being observed in various sensitive regions. As with the other models, its applicability is relatively untested for regions where acidic inputs are moderate and pH shock effects are intermediate in significance.

The final section, entitled Concluding Comments and Research Needs, is a brief statement on the data needed to achieve an effective validation of the sensitivity measurement approaches. Insufficient data presently exist for fully quantifying hydrogen ion or sulfate fluxes through a wide variety of watersheds, or aluminum mobilization during peak H^+ concentrations. Nutrient stripping effects on forest productivity, effects on

mammals and predatory birds from metal mobilization and food chain alterations, and the role of organic matter in mediating acid deposition effects are all too poorly known to have a fully reliable, locally applicable sensitivity measure at this time.

SECTION III

SUB-COMPONENTS OF LAKE/WATERSHED SENSITIVITY

Richard Miller, Roland Usher, Orie Loucks and William Swanson

Devising an adequate measure of forest, watershed and lake sensitivity to combinations of pollutants requires an understanding not only of the response mechanisms, but also of various processes occurring within the system which might mediate or interact with the effects of acidic deposition. Within the lake/watershed system these processes include water flow, nitrogen and sulfur cycling, alkalinity production, interactions with organic material, nutrient stripping (leaching), H+ toxicity, mobilization and toxicity of aluminum and heavy metals, and synergisms between H+, aluminum and heavy metals.

Figure III-1 is an expanded version of Figure I-1 and is meant to put all the sub-components of forest, lake and watershed sensitivity into perspective. The scheme is obviously complex and highly linked; changes in one place have effects elsewhere. Systems of differing overall sensitivity are indicated, and fluxes from the different systems will vary from zero in the highly buffered areas to generally high fluxes in systems undergoing alteration (Overrein 1980). The events occurring following watershed deposition are discussed below.

WATER FLOW PATTERN

The pathways by which water flows through a watershed are implicit in Figure III-1 and are of crucial importance to acidification by determining the contact time between acid inputs and potentially neutralizing soil constituents. A considerable amount of surface runoff will greatly increase the through-put of acid directly to the aquatic components of the system. The exact flow patterns depend on a variety of factors, including topography and slope, soil type, rate of input and vegetative cover.

Two types of water flow exist: surface flow and sub-surface flow. Surface flow is water movement across the top of the soil to an arbitrary depth of 2 cm. This flow can be interpreted in two ways: dynamic and continuous. Dooge (1973) has developed mathematical equations describing surface flow that take into account flow velocity, slope, friction of slope, depth of flow, flow velocity/unit area, length of slope, length of flow, outflow, outflow equilibrium, time, characteristic time dependent on flow intensity, and duration of uniform flow. Predicting the flow rate of water through the surface soil is important because this layer has the most biological activity and is therefore one of the most influential components of the system.

Sub-surface flow is the movement of water through the soil profile below the surface. This aspect of hydrology is perhaps the most difficult to accurately simulate in mathematical form. The movement of water can proceed in two directions: (1) percolation (downward movement to the

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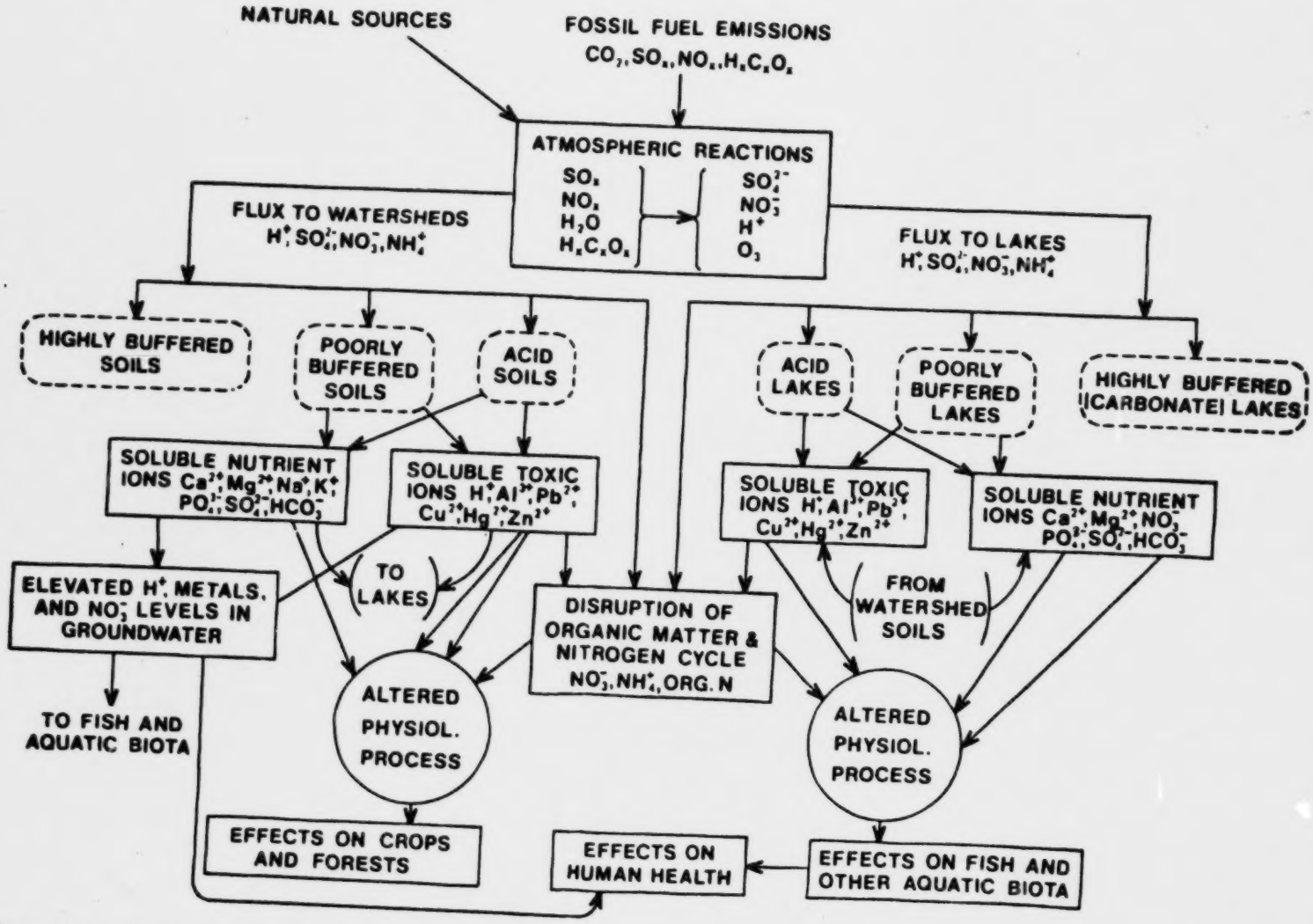

Figure III-1. Flow diagram showing system linkages for acid precipitation formation, deposition and effects as a consequence of nitrogen and sulfur oxide emissions from fossil fuel combustion.

groundwater), and (2) capillary rise (upward movement from the groundwater). Implicit in both directions of flow is equilibrium between the water and the soil. Mathematical equations describing percolation have been developed that take into account such factors as soil suction, hydraulic conductivity, hydraulic diffusivity, soil moisture content and elevation above water table.

The above discussion has dealt with the liquid form of precipitation only. The solid form, snow, does not contribute to waterflow until snowmelt occurs. Light (1941) has proposed a complex but realistic approach for predicting snowmelt that takes into account many of the major microclimatic variables that can influence snowmelt.

Once the snow is in liquid form it can be placed into the surface and sub-surface flow equations. Wright and Dovland (1977) have discussed the problems associated with snowmelt, snowpacking and major ion concentrations in Norway. Fahey (1979) and Wright and Dovland (1977) imply that slow input of acid, metals and ions from the snow into the watershed occurs as a result of snowmelt. One question that has not been properly addressed in the literature is the importance of snowmelt and soil contact with the water before it enters the lake and/or river, as it pertains to acid and heavy metal inputs to the watershed.

Finally, Glass et al. (1981) note that because, in northern soils, the sulfate ion is a relatively conservative substance (Harvey et al. 1981), high rates of evaporation can leave the precipitation sulfate concentrated in the soil solution (and lake water) by a factor controlled by evaporative losses. The equations for lake sulfate concentrations developed by Henriksen (1980, see later sections) show this factor, plus the dry deposition, to be 1.9 for central Norway. Regions of proportionately higher evaporative losses have higher observed sulfate concentrations in lake water than are predicted by the Henriksen equations. These processes vary with precipitation and temperature patterns between regions and, in areas of strong topography, from one watershed to the next.

NITROGEN CYCLING

Because large quantities of ammonium and nitrate can be present in precipitation, it is of interest to discuss their relationship to acidification. First, a brief review of the natural reactions of the nitrogen cycle will help in understanding the possible fates of added ammonium and nitric acid.

Atmospheric nitrogen (N_2) is reduced by the soil microflora, collectively termed nitrogen fixers, to ammonia (NH_3). The NH_3 is hydrogenated in the soil system to the ammonium ion, NH_4^+, resulting in a loss of $1H^+$ from the soil system. The NH_4^+ either may be assimilated by plants (resulting in an input of $1H^+$, thus balancing previous output), or it may be oxidized to nitrate (NO_3^-) forming $2H^+$. The ammonium ion assimilated by plants will eventually be returned to the soil system as NH_3. The following reactions simplify the oxidation of NH_4^+, a process termed nitrification:

$$NH_4 + 1\tfrac{1}{2}O_2 \rightarrow 2H^+ + H_2O + NO_2^- \qquad \text{(eq. 1)}$$

$$NO_2^- + \tfrac{1}{2}O_2 \rightarrow NO_3^- \qquad \text{(eq. 2)}$$

Nitrate is generally taken up by plants, resulting in an input of 1 OH- ion to the system, but under anaerobic conditions it may be reduced to nitrite (NO_2-), summarized in equation 3:

$$NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O \qquad \text{(eq. 3)}$$

The nitrite (under anaerobic conditions) may be further reduced to nitrous oxide (N_2O) or atmospheric nitrogen (N_2). Both of these reactions consume H+ ions from the soil system. The magnitude of H+ consumption by the process of nitrate conversion to N_2 (denitrification) is largely unknown for most terrestrial ecosystems. These reactions probably occur more readily in aquatic systems, where anaerobic conditions more frequently occur.

The molecular forms of nitrogen deposited in acid rain can result in either acidification or neutralization of surface waters. Nitrogen as nitrate ions (NO_4-) can be incorporated directly by plants, and the resulting reactions with water release hydroxyl ions (OH-) into the environment (Figure III-2). The hydroxyl ions can raise the pH of the soil and water or neutralize the hydrogen ions of the nitric acid. Natural decomposition of nitrogenous plant materials also releases hydrogen ions, but net accumulation of plant tissue dominates in most ecosystems; hence net production of neutralizing capacity from nitrate addition is usually dominant.

Several scenarios operating in terrestrial and/or aquatic systems involving ammonium and nitrate inputs and acidification are possible:

(1) If all nitrogen in precipitation is in the form of HNO_3, or if the concentration of HNO_3 is much greater than the concentration of NH_4+, and if all nitrogen is assimilated, then a decrease in the acidity of the system is possible. (The H+ associated with NO_3- may be neutralized by the OH- released when nitrate is assimilated).

(2) If the HNO_3 concentration equals the NH_4+ concentration and if there is no leaching, then there may be a slight increase in the acidity of the system. (The H+ from HNO_3 may be neutralized when NO_3- is assimilated; the NH_4+ adds 1H+ to the system).

(3) If all the nitrogen in rain is in the form of NH_4+, or if the NH_4+ concentration is much greater than the NO_3- concentration, and if there is no leaching, then an increase in the acidity of the system will occur.

(4) If HNO_3 predominates in precipitation, and if leaching occurs, then an input of H+ to the system will occur.

(5) If NH_4+ predominates in precipitation and if assimilation does not occur, three routes are possible:

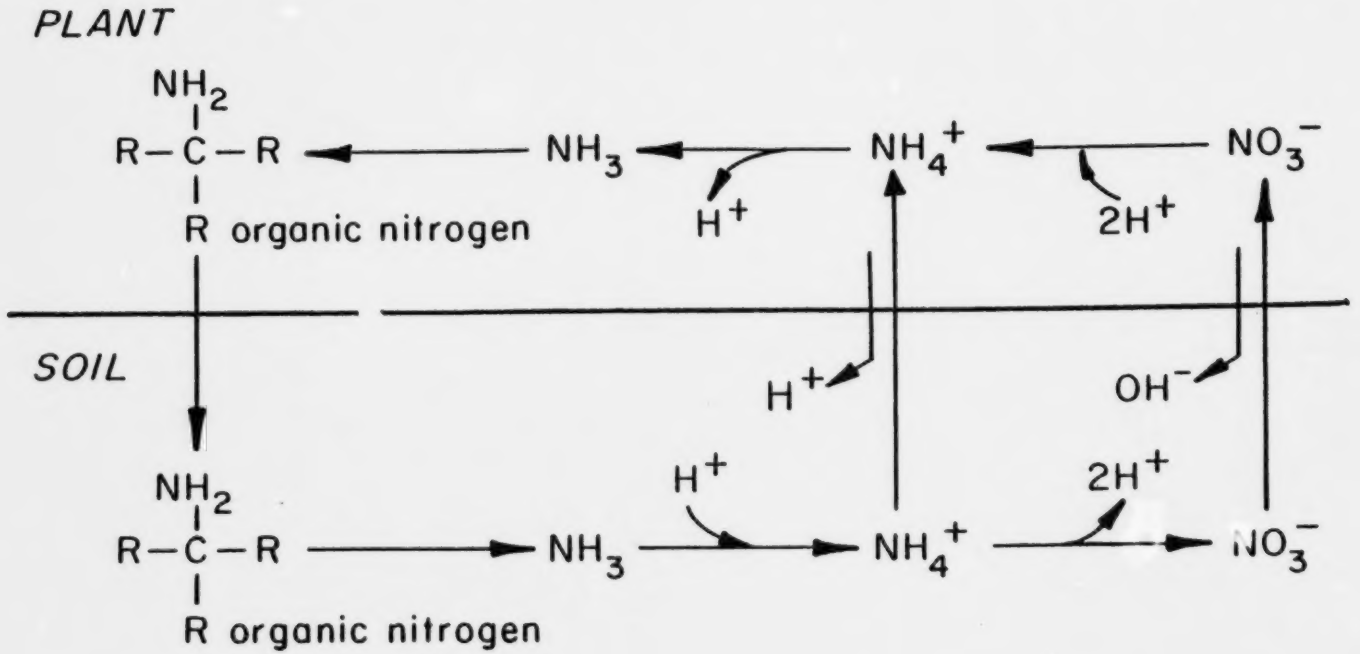

Figure III-2. Simplified nitrogen cycle showing acid-forming and acid-consuming reactions. Assumes all N utilized as NO_3-. From Reuss 1976.

(a) Leaching of NH_4^+ intact (acidifies receiving water);

(b) conversion to NO_3^- and then leaching, adding $2H^+$ to the system; or

(c) exchange reactions on soil colloids between NH_4^+ and soil cations, resulting in cation stripping and loss of nutrients from the soil system.

What route incoming nitrate or ammonium will take depends on a variety of factors, including: soil type (base saturation, cation exchange capacity and mineralogy); vegetation type, density and nutrient condition; and water flow patterns.

One further impact of acid deposition on the nitrogen cycle is a possible disruption of the rate (and quantity) of nitrogen cycled. Many steps of the nitrogen cycle (i.e., nitrogen fixation, ammonification, nitrification and denitrification) are mediated by microorganisms known to grow only in conditions above a pH of approximately 5.0. Acid conditions are known to inhibit modulation of legumes (Andrew 1978; Evans et al. 1980), resulting in a decreased nitrogen fixation rate. Besides direct injury to organisms involved, acid deposition could lead to a decreased availability of molybdenum, which is an essential constituent of the enzymes involved in nitrogen fixation, nitrification and denitrification. Because nitrogen is such a critical plant nutrient, any disruption of the nitrogen cycle could have severe consequences in terms of plant productivity.

SULFUR CYCLING

Large quantities of sulfur are being added to terrestrial and aquatic ecosystems via precipitation. It is important to determine what is the fate of this added sulfur in terms of acidification. A brief review of the sulfur cycle is in order.

The predominant form of sulfur in the soil system is organic sulfur, generally in the S^{2-} state or as sulfide, elemental sulfur, thiosulfate, tetrathionate and sulfite (Reuss 1975). This sulfur is oxidized to sulfate by autotrophic and heterotrophic microorganisms. Autotrophic bacteria of the genus Thiobacillus are recognized as the most important group of sulfur-oxidizing microorganisms. Five species predominate: T. thioparus, T. denitrificans, T. thiooxidans, T. ferroxidans, and T. novellus. T. ferrodoxins and T. novellus are found in acid soils, even down to pH 2.0. Regardless of the pathway or microorganism involved, the oxidation of sulfides or sulfur results in the formation of H+:

$$S + 3/2\ O_2 \quad H_2O \rightarrow SO_4^{2-} \quad 2H^+ \qquad \text{(eq. 4)}$$

$$H_2S + 2O_2 \rightarrow 2H^+ + SO_4^{2-} \qquad \text{(eq. 5)}$$

Under anaerobic conditions (primarily deltas and flooded systems), sulfur may be reduced to sulfides by members of the genera Desulfovibrio and Desulfotomaculum. Iron sulfides often accumulate in such areas.

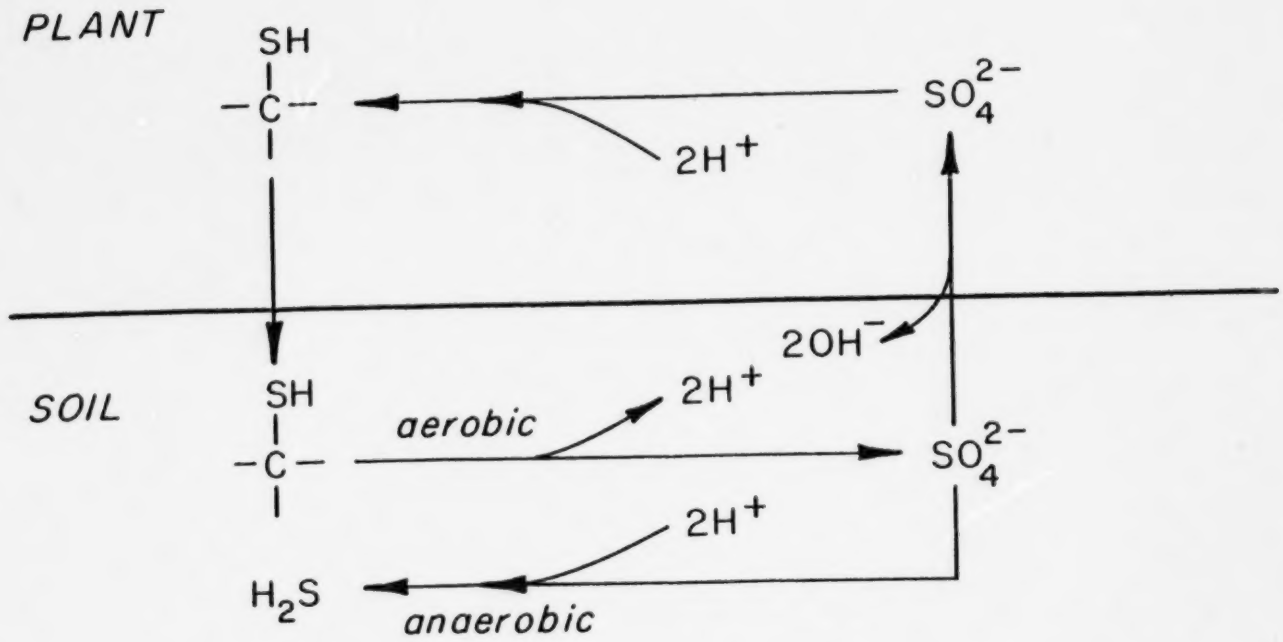

Figure III-3. Simplified sulfur cycle illustrating acid-forming and acid-consuming processes. (From Reuss 1976.)

A simplified sulfur cycle in Figure III-3 shows the acid-forming and acid-consuming reactions (Reuss 1976). As shown, the sulfur cycle is balanced and no net change in acidity should occur. (The 2H+ ions produced when organic S is oxidized to SO_4^{2-} are neutralized by the 2 OH- ions released when the plant incorporates the SO_4^{2-}. The 2 OH- ions lost are balanced when 2H+ ions are used to reduce SO_4^{2-} to organic S in the plant system.) However, because of lags between sulfate formation and plant uptake, the H+ ions produced will displace basic cations from exchange sites, and the cations plus SO_4^{2-} will leach through the system. Sulfate reduction by anaerobic heterotrophs occurring in flooded areas results in neutral or basic soils as H+ is consumed. Such soils will become acid if they become aerobic due to the oxidation of sulfides to sulfates. Sulfur entering the soil system as S^0, SO_2, H_2SO_3 or H_2SO_4 will lead to the same net increase in acidity (2H+) only if the sulfate produced is not immediately absorbed by the plant system (i.e., if sulfur is in abundant supply). If sulfur is in short supply, no acidification will occur because the 2 OH- ions released will balance the 2H+ ions produced.

In spite of many possible reactions, much of the sulfate deposited in acid precipitation is not retained in the Precambrian Shield watersheds, thus functioning freely as an anion balancing the transport of H+ in surface water and shallow groundwater. The amount of sulfate in runoff from the Shield areas is very close to the amount deposited. At the Experimental Lakes Area in Ontario, Schindler et al. (1976) found virtually 100% of the atmospheric SO_4^{2-} input in the runoff. Likens et al. (1977) found 67% of the total input in runoff at Hubbard Brook, New Hampshire, and Harvey et al. (1981) found 25% more sulfate in runoff from four watersheds than was measured in the bulk deposition. This "excess" sulfate may be due to unmeasured inputs by dry and gaseous deposition.

Ultimately, excess sulfate can be leached through the poorly-buffered soils of these regions in association with cations released from exchange sites. Sulfur taken up by plants (or SO_2 absorbed by foliage) is subsequently reduced to the sulfide state (primarily as amino acids) during decomposition, thus returning to an initial state of the sulfur cycle (Figure III-3).

ALKALINITY

One of the most important factors influencing the sensitivity of lakes to acid input is alkalinity, or the capacity of the water to neutralize acid. It is normally measured by titrating a water sample with acid to a fixed end-point, depending on total inorganic carbon concentration. Carbonate and bicarbonate are the major contributors to alkalinity in most natural waters, but other anions of weak acids (e.g., organic anions) can also accept protons.

Lake alkalinity is largely a function of the type of rock and biological activity (soil layer CO_2 production) in the drainage basin. If carbonates are present, weathering by acid will release bicarbonate into the water as the major buffering agent. In this case alkalinity can be high, and the lake will be insensitive to acid input. In the absence of carbonate minerals, bicarbonate can be released by weathering of other

minerals, but the quantities are slight. On granitic substrates, very little alkalinity will be made available by weathering, and the main sources are from carbonic acid, as controlled by CO_2 concentrations in the soil (e.g., see Johnson et al. 1977). Lakes in such areas will often be very poorly buffered (Wright and Henriksen 1978, Glass and Loucks 1980).

There may be some alkalinity produced in the anaerobic hypolimnion of small lakes. Cook and Schindler (1980) report increasing bicarbonate and ferrous iron during summer stratification due to the oxidation of organic matter to CO_2 and the reduction of ferric iron. Hutchinson (1957) notes a similar phenomenon in a number of lakes and explains that ferrous and manganous bicarbonates may diffuse from the sediments and add noticeably to alkalinity in softwater lakes.

Kramer (1976) has reviewed the relationship between pH and alkalinity in lakes. Water in equilibrium with $CaCO_3$ has pH 8 and about 2 meq/ℓ of alkalinity. The pH and alkalinity levels drop as this solution is diluted, but between pH 4 to 6, alkalinity remains nearly constant at 0.1-0.2 meq/ℓ. Kramer attributes this buffering to alumino-silicates, FeOOH and soluble organic acids. He concludes that low alkalinity lakes in non-calcareous terrain are likely to be altered by acid rain, but that detailed analysis of soil minerology at all depths is necessary to accurately assess the risk.

ORGANIC INTERACTIONS

The role of organic materials in soils and water as they affect the impact of acid deposition has been the subject of some speculation but little quantitative study. This is a major oversight since organics may influence almost all the reactions relating to acidification. Of course, the formation of humic acid substances is one of the factors leading to natural soil acidification. Acid deposition can be seen as an addition to this process, so the role of organics deserves consideration.

One of the major characteristics of humic substances in soils is their behavior in cation exchange. McFee et al. (1976) list the average cation exchange capacity of humus as 200 meq/100g. This can serve as a significant buffer for added H+ in precipitation. If base saturation is high, the added H+ will exchange for cations absorbed to the organic matter, such as Ca^{2+} and Al^{3+}. Organic soils with lower base saturation are already acid, and H+ in rainfall will have little additional effect (Petersen 1980).

Another characteristic of organic materials is their ability to chelate various ions. These ions may then either be retained in the soil or leached out, depending on the behavior of the organic molecule. Schnitzer (1980) notes that moderate acidity will decrease the solubility of humic acids but increase the solubility of fulvic acids, which may then be lost from the soil system with their absorbed ions. Organic chelation and mobilization could be a significant factor in ion mobilization from watershed soils, but the quantitative effects are unknown.

Once into the aquatic system, dissociated organic acids may add to the alkalinity of the system by their ability to take up H+ (Chen et al. 1978):

$$R\text{-}COOH = RCOO^{-} + H+$$

This reaction may be especially important in waters where bicarbonate buffering is low, and organic concentrations are high. The buffering by this reaction will probably occur at pH less than 5.

One final effect of organics relative to acidification problems is the chelation of toxic metals. Baker and Schofield (1980) have observed that aluminum chelated with organics is not toxic to fish. Similar detoxification is possible with other metals mobilized by acid deposition, e.g., Hg, Cd, Cu, etc.

Quantitative determination of the role of organics in lake/watershed sensitivity to acid deposition will depend on the amount of organics present, and the quantitative effect on the processes discussed above. Various methods are available to measure organic content depending on the medium: soil or water. Total organic matter in soil can be determined by combustion of dried samples. Various organic fractions can be extracted by treatment with acid or alkali as described by Schnitzer (1980). Both humic and fulvic acids dissolve in alkali, then humics can be precipitated by subsequent acid treatment. This allows separate determination of the quantity of organic material in each fraction. Specific organic molecules or classes of molecules (e.g., amino acids) may be separated and quantified by various techniques, including GC, GLC and spectrophotometry.

Organic matter dissolved in water can be determined by oxidation to CO_2, followed by infrared absorption measurement of CO_2. This quantifies total organic carbon (TOC). Natural waters can also be analyzed by UV absorption as an indication of relative organic content, but this would not be as accurate as TOC analysis. Other methods include color comparisons with standards and methods for specific compounds as indicated above. Each method has advantages and disadvantages: TOC analysis is accurate but time-consuming and non-specific, while color comparisons are quick but difficult to relate to actual organic content. The choice of a suitable method depends on the relationship between quantity and effect, e.g., how much organic matter and what type is necessary to chelate and detoxify aluminum at various concentrations.

CATION NUTRIENT STRIPPING

Nutrient stripping is one of the most serious consequences of acid deposition because loss of critical nutrients from the soil system may be expressed in lowered growth rates and reduced productivity. Abrahamsen et al. (1976), working with podsol and podsol-brown earth lysimeters, documented the effects of hydrogen ion concentration on nutrient leaching. For the podzol-brown earth lysimeters, net losses of Ca, Mg, Al and sulfate occurred; whereas in the podsol lysimeters, net losses occurred for Ca, Mg, Al, and K, (Figures III-4 and III-5). For all elements except Al in the podsol-brown earth lysimeters, increasing hydrogen ion concentration resulted in increased leaching of nutrients.

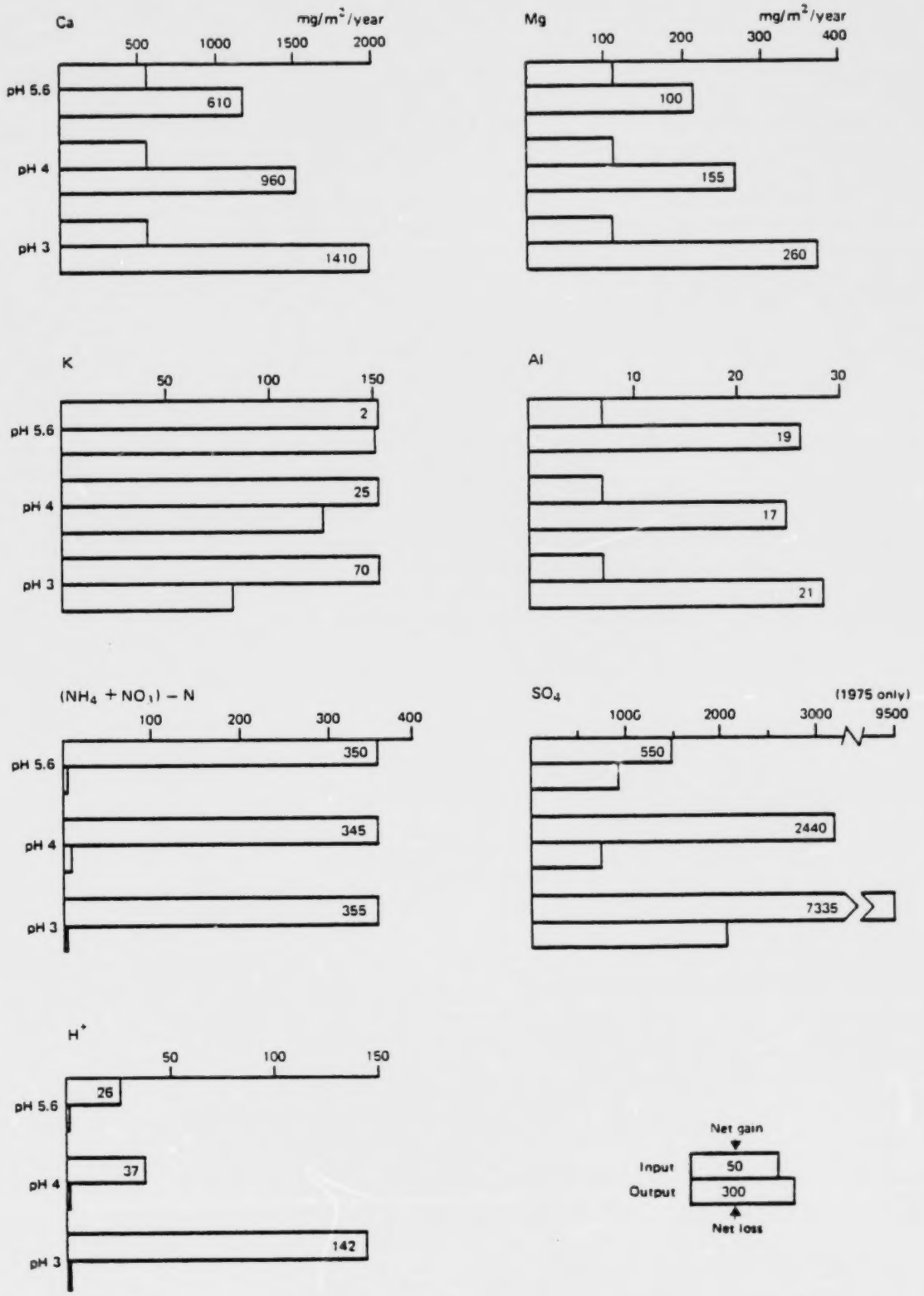

Figure III-4. Nutrient budgets for podzol-brown earth lysimeters treated with artificial rain of pHs 3, 4, and 5.6. (From Abrahamsen et al. 1976.)

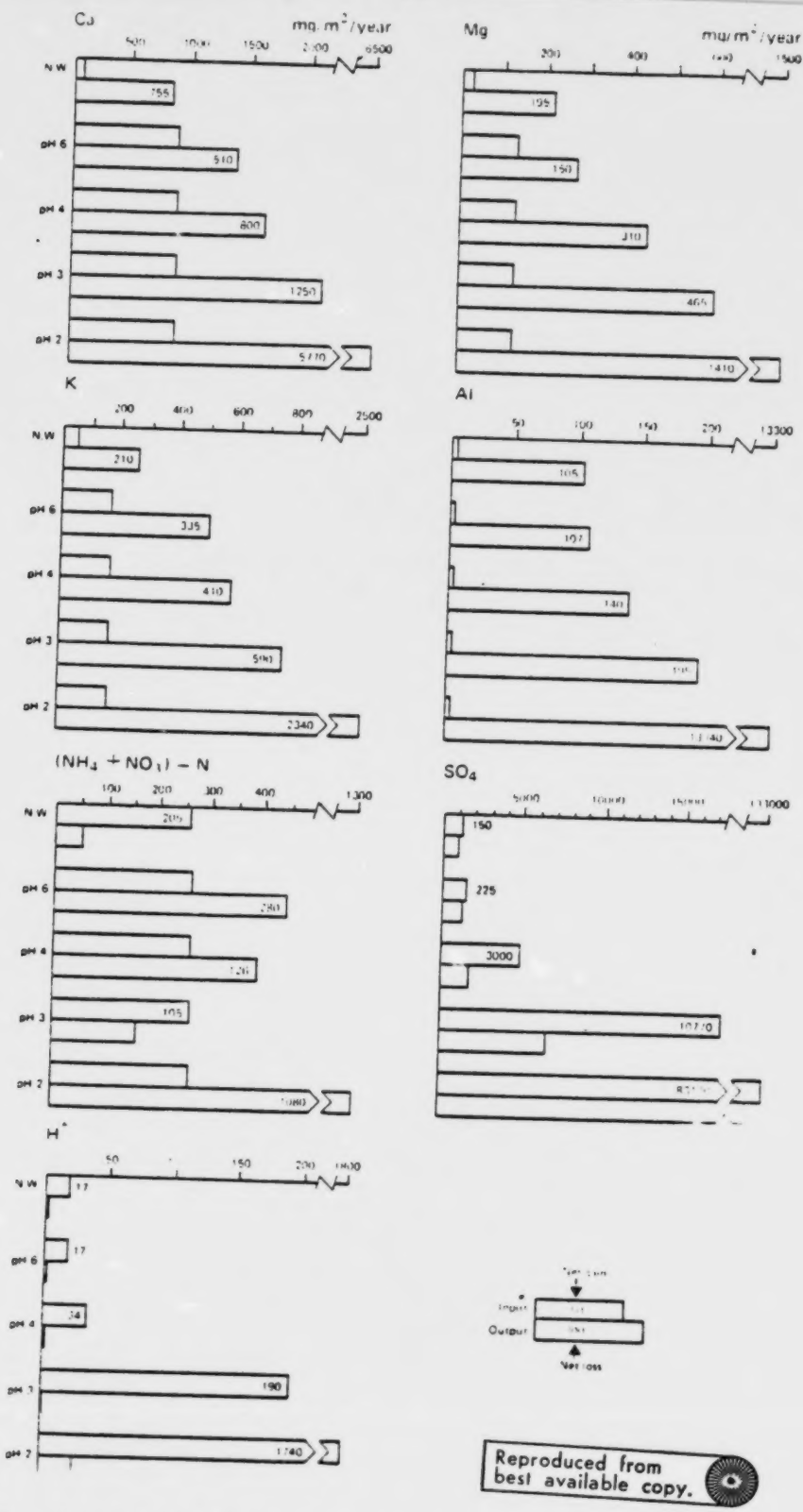

Figure III-5. Nutrient budgets for podzol lysimeters treated with simulated rain of pHs 2, 3, 4 and 6. N.W. = not watered; received incident rain of Norway, pH 4.4. (From Abrahamsen et al. 1976.)

At Mt. Moosilauke, New Hampshire, Cronan (1980) found sulfate to be the major anion in precipitation, throughfall, percolate and springwater; aluminum the major cation in springwater; and hydrogen the major cation in precipitation, throughfall and percolate. Potassium is readily leached from the forest canopy (as is calcium) but is rapidly taken up by the vegetation. Harvey et al. (1981) also note potassium retention by vegetation in Canadian watersheds. Calcium is also retained to a certain extent in the soil system, although more than half of the throughfall concentration is found in percolate and springwater (Table III-1). Magnesium concentrations were highest in the springwater and lowest in precipitation.

Harvey et al. (1981) have summarized nutrient budgets for several Canadian watersheds (Table III-2). All watersheds studied have a net output of major cations (ΣCa + Mg + Na + K) except for Clear Lake. The ELA and Harp Lake results are of comparative interest (in terms of effects of H ion input) as they both have similar bedrock geology and soil types. The increased H inputs at Harp Lake have resulted in increased leaching rates of Ca + Mg. Harvey et al. note that on the basis of the limited evidence available, it appears that the increased H+ input to southern Ontario has resulted in a 2- to 4-fold increase in net output of cations.

There are numerous problems associated with quantifying nutrient leaching from the soil. These include (1) organic composition, content and percentage in the soil (see Goring and Jamaker 1972); (2) pH-dependent CEC sites (Clark et al. 1966); (3) the buffering capacity of ions other than Ca^{2+} and Mg^{2+} (DeVilliers and Jackson 1967, Turner and Clark 1965, Clark and Turner 1965, Clark 1966); and (4) the toxicities of ions (Clark 1966, McCormick and Steiner 1978, Cronon and Schofield 1979). The two areas that have the most influence with regards to acid precipitation are (1) organics and (2) pH-dependent CEC sites.

Currently there are only a few general equations that deal with the complexity of nutrient leaching. The parameters for these equations are molar ion concentrations denoted by "[ ]" and ion activities denoted by "( )". Addiscott (1977) and Reuss (1978) have proposed simplified models describing the dynamics of nutrient leaching. Reuss' model will be outlined and discussed briefly.

Reuss utilizes (1) sulfate (SO_4^{2-}) absorption, (2) H+ and HCO_3^- equilibria, (3) Ca^{2+} and H+ equilibria, (4) Al^{3+} equilibrium, and (5) electrical neutrality. This proposed model assumes that there is a low Ca^{2+} base saturation and a low exchangeable Ca^{2+}/unit soil. The level of SO_4^{2-} is an indicator of H+ input and can be expressed as:

$$SO_4^{2-}\text{ (sorbed)} = K_m\,[SO_4^{2-}] \,/\, K_{\frac{1}{2}} + [SO_4^{2-}] \qquad \text{(eq. 6)}$$

where K_m is the number of moles of SO_4^{2-}/unit soil at saturation and $K_{\frac{1}{2}}$ is equal to $\frac{1}{2}\,K_m$. The total SO_4^{2-} present can be expressed as:

$$SO_4^{2-}\text{ (total)} = SO_4^{2-}\text{ (sorbed)} + SO_4^{2-}\cdot\theta\cdot D \qquad \text{(eq. 7)}$$

where θ is the volumetric moisture content and D is soil depth. Equations (6) and (7) express the balance of SO_4^{2-} between the soil and the soil

TABLE III-1. Mean and median concentrations of dissolved ionic materials in bulk precipitation, canopy throughfall, forest floor and A_2 horizon percolate, and springwater during the 1975 and 1976 growing seasons at the Mt. Moosilauke subalpine sampling sites, New Hampshire. Springs also include 1977 data. (From Cronan 1980.)

	Concentration (micro-equivalents per liter)																
Sample	pH	H^+	Ca^{2+}	Mg^{2+}	K^+	Na^+	NH_4^+	Al	Fe^{2+}	Mn^{2+}	Total Cations	SO_4^{2-}	Cl^-	NO_3^-	HCO_3^-	Total Anions	Anion Deficit*
Bulk precipitation	4.08	83	9	3	3	4	13	2	1	0	118	75	7	21	0	103	15
Throughfall																	
mean	4.02	95	36	14	37	3	6	5	1	4	201	143	13	12	0	168	33
summed equivalents	-	-	4	1	3	0.2	0.5	2	0.4	0.7	-	11	1	2	-	-	-
median	-	-	20	8	28	3	5	5	1	4	-	117	11	8	-	-	-
Percolate																	
mean	4.04	91	25	15	16	7	5	54	4	2	219	137	16	8	0	161	58
summed equivalents	-	-	2	1	2	0.3	0.7	4	0.3	0.2	-	3	1	1	-	-	-
median	-	-	22	15	10	5	3	51	4	2	-	132	13	5	-	-	-
Springs																	
mean	4.66	22	26	19	10	13	3	67	2	1	163	132	7	15	0	154	9
summed equivalents	-	-	0.5	0.6	0.3	0.7	0.7	3	1	0	-	2	0.3	3	-	-	-
median	-	-	25	18	11	13	3	67	2	1	-	131	7	14	-	-	-

* The anion deficit is presumed to represent organic ligands; this has been confirmed on the basis of GLC and ultra-violet irradiation experiments.

TABLE III-2. Net export of major ions (meq m^{-2} yr^{-1}) for calibrated watersheds in Canada (From Harvey et al. 1981).

Watershed	Net Export (meq m^{-2} yr^{-1})									Input of H+ (meq m^{-2} yr^{-1})
	Ca^{++}	Mg^{++}	Na^{+}	K^{+}	ΣM	NH_4^{+}-N	NO_3^{-}-N	HCO_3^{-}	SO_4-S	
Carnation Creek, Vancouver Is.	269	61.2	118.5	5.8	454.5	-7.7	-4.3	270.0	131.4	1-3
Jamieson Creek, B.C.	171.6	54.5	53.9	4.3	284	-0.2	-2.2	48.7	4.9	-
Haney, S.W. B.C.	70.4	22.2	29.4	2.0	124	-8.8	-13.4	approx. 200	18.0 (range 3.1-47)	~80
12 watersheds, ELA, Western Ontario	[1]36.6 [2]17.7	24.0 16.4	18.0 11.1	3.4 0.5	82.0 45.7	-0.9	-0.8	-	38.8	est. 7-10
Rawson Lake Watershed, Western Ontario	11.2	12.1	9.0	0.4	32.7	Total N reported			0.9	~7-10
4 subwatersheds of Harp Lake; Haliburton-Muskoka, Ontario	52.7	33.0	6.6	2.3	94.6	-30.2	-32.3	31.7	43.9	67
Clear Lake, Haliburton	-36.8	-25.3	1.3	-0.4	-61.2	NO_3^{-}+NH_4^{+} retention = 62.1				

[1] Gross output

[2] Estimated net output using input in precipitation from Rawson Lake watershed studies.

solution. This balance can be interpreted as SO_4^{2-} retention or holding capacity of the soil system which has obvious implications for buffering capacity related to the sulfur cycle.

Distilled water in equilibrium with atmospheric CO_2 should have a pH of 5.6. Therefore, it is necessary to express the equilibria between H+ and HCO_3^-. This can be expressed as:

$$(H+) + (HCO_3^-) = (CO_2)g \cdot 10^{-7.81} \cdot \qquad \text{(eq. 8)}$$

The balance between Ca^{2+} and H+ is an indicator of the buffering capacity. Reuss assumes that the input of Mg^{2+} is insignificant in relation to the Ca^{2+} input. Therefore, the equilibria is expressed as

$$pH - \tfrac{1}{2}\, pCa = K_L \qquad \text{(eq. 9)}$$

which is simplified from Schofield and Taylor's (1955) "Lime Potential" { $K_L = pH - \frac{1}{2}p(Ca + Mg)$ }. Equation (9) can be modified to include the exchangeable Ca^{2+}, Ca^{2+} in solution and the CEC.

The Al^{3+} equilibrium can be expressed as

$$(Al^{3+}) \cdot (10^{-14} / (H^+))^3 = K_{Al} \qquad \text{(eq. 10)}$$

and is pH dependent

(DeVilliers and Jackson 1967).

There must also be an electrical balance between the soil and soil solution. This balance is a function of molar ion concentration and ion activity. The electrical balance can be expressed as

$$[H+] + 2[Ca^{+2}] \quad 3[Al^{+3}] = 2[SO_4^{-2}] + [HCO_3^-] + [Cl-]. \qquad \text{(Eq. 11)}$$

It appears from the literature that Reuss' simulation model may be applicable to acid precipitation-sensitive systems only; however, as Reuss states, the model needs verification in the field and in the laboratory. This model deals superficially with (1) the input/output and neutralization of H+ and (2) the variability of the organics.

HYDROGEN ION TOXICITY

General Reactions of H+

Exchanges of H+ through the watershed depend largely on soil characteristics, the balancing anions, and water flow patterns. Soils with high pH usually are well buffered by carbonates or have high base exchange capacity to balance anions, and have little flux of H+ or mobile anions to surface waters. As soil pH, base saturation and/or cation exchange capacity decrease, the likelihood that H+ and a mobile anion will pass through in the soil water greatly increases (Wiklander 1980). In very acid soils, almost no H+ will be retained by the soil. In general, podzolic soils should be most susceptible to much alteration by acid inputs,

(Petersen 1980), but exchangeable cations and water flow can modify the results (Johnsen and Freedman 1980). Some podzols may contain appreciable cations to exchange for H+, depending on inputs. In addition, water flow through the system may occur too quickly at times for complete exchange to occur. Bache (1980) points out that soil texture and intensity of rainfall are important factors determining the opportunity for H+ uptake by soils. One further factor affecting H+ movement through watershed soils is sulfate retention (Johnson 1980). Cation movement requires the movement of balancing anions, so that if sulfate is retained and other anions are not mobilized, then H+ cannot be leached. Soils with a high percentage of sesquioxides are likely to be resistant to sulfuric acid leaching.

The toxic effects of elevated H+ ion concentrations have been known over a considerable period, for both terrestrial and aquatic ecosystems. Acid soils are known to be infertile (Hewitt 1952), mainly because of adverse concentrations of nutrients and elements (Andrew 1978), and the known lower production rates of acid lakes (EIFAC 1969).

Because, at low pH, the H+ ions also may displace aluminum and heavy metals from exchange sites, it is reasonable to assume that all three can occur simultaneously, at least during peak mobilization events. Synergistic effects of these three pollutants are thus a potential result of acid deposition. Some research has been conducted in the area of synergisms, but more is needed, especially with terrestrial organisms.

Terrestrial Effects

Hewitt (1952) has summarized the factors affecting crop productivity in acid soils:

(1) Direct injury to below-ground organs by hydrogen ions.

(2) Indirect effects of low pH:

  (a) Physiologically impaired absorption of calcium, magnesium, and phosphorous.

  (b) Increased solubility, to a toxic extent, of aluminum, manganese, heavy metals and possibly iron.

  (c) Reduced availability of phosphorus partly by interaction with aluminum or iron, possibly after absorption.

  (d) Reduced availability of molybdenum.

(3) Effects from the low base status:

  (a) Calcium deficiency.

  (b) Deficiencies of magnesium, potassium or possibly sodium.

(4) Induced abnormal biotic factors:

(a) Impaired nitrogen cycle.

(b) Impaired mycorrhizal activity.

(c) Increased attack by certain soil pathogens, e.g., "club root".

(5) Accumulation of soil organic acids or other toxic compounds.

These same factors could affect forest and lake productivity, and many of them could be induced by acid precipitation, depending on the buffering capacity of the system.

Aquatic Effects

The elevated H^+ ion concentration in lakes where bicarbonate buffering is negligible, or has been eliminated by acid inputs, is now being linked with adverse effects on numerous fish species, and on phytoplankton and zooplankton species. Hall and Likens (1980) have presented data suggesting that the emergence of adult mayflies, stoneflies, caddis flies and some true flies decrease in part due to lower pH, although elevated levels of Al^{3+}, Ca^{2+}, Mg^{2+}, K, Mn^{2+}, Fe, and Ca^{2+} were present. Although many parts of aquatic ecosystems are detrimentally affected by acidic conditions, our discussion will focus on the effects on fish.

Laboratory experiments and field data are in general agreement concerning effects of pH on fish (Table III-3), but only in cases where toxicity is not complicated by the presence of ferric salts (EIFAC 1969). Although factors other than hydrogen ions often make it difficult to identify the cause of the observed response, the development of a pH below 5 (or above 10) is considered to be unsafe for fish (Table III-4). Fromm (1980) notes that a pH around 6.5 is the 'no effect' level of pH effects on fish reproduction. A pH between 5 and 9 is generally agreed as being safe for fish. However, some species of fish can tolerate pH values lower than those reported in the laboratory to be lethal, which suggests that long-term acclimation is possible (EIFAC 1969).

A generally agreed observation in the literature is that early stages of fish development are much more sensitive to acid stress than adult stages. Thus, acid deposition in sensitive lakes characteristically results in a failure to replace the older age classes; eventually the fish population is eliminated.

Most researchers also agree that sodium imbalance is the dominant cause of death, although Packer and Dunson (1970) contend that death is attributable to lowered blood pH. The ameliorating effect of high levels of Ca on toxicity at low pH is probably a result of reduced sodium loss from fish (Wright and Snekvik 1978). Fromm (1980) has reviewed the physiological and toxicological responses of freshwater fish to acid stress. There is some question whether H+ ions alone are toxic at the observed concentrations, but the development of low pH is a major factor in lake sensitivity.

TABLE III-3. LITERATURE SURVEY ON pH TOXICITY TO VARIOUS FISH SPECIES.

Fish species	pH level	Effect and Comments	Reference
Salmon and Trout	5.5	"critical to young"	Sunde 1926 as cited Hagen & Langeland 1973
Salmon and Trout	5.3 & lower	"highly lethal"	Sunde 1926 as cited Hagen & Langeland 1973
Salmon	5.0	Lethal to 90% of eyed eggs	Johansson et al. 1977
Salmon	5.0-5.5	Critical range for hatching	Bua & Snekvik 1972 as cited Hagen & Langeland 1973
Salmon	4.5	LD_{50} in 12 days to yolk sac fry	Dahl 1927 as cited EIFAC 1969
Salmon Salmon	4.59 4.34	96% Hatching success 48% Hatching success	M. Grande personal comm. as cited EIFAC 1969
Atlantic Salmon	4.3	LD_{50} of embryos and alevins	Daye and Garside 1979
Atlantic Salmon	4.49	50% mortality of yolk sac fry in ~9.0 days	Grande et al. 1978
Atlantic Salmon	5.8-6.2	Lethal pH in 2-day test; possible CO_2 interaction	Bishai 1960 as cited EIFAC 1969
Atlantic Salmon	4.0-5.0	Delayed hatching	Peterson et al. 1980
Atlantic Salmon	4.0-4.2	Hatching prevented	Peterson et al. 1980
Trout	>5.0	High and probably total lethality	Dahl 1926 as cited Hagen & Langeland 1973
Trout	4.5	Critical range for hatching	Dua and Snekvik 1972 as cited Hagen & Langeland 1973
Trout	4.7-5.4	80% yolk sac died in 20 days	Dahl 1927 as cited EIFAC 1969
Trout	5.1-5.7	10% yolk sac died in 20 days	Dahl 1927 as cited EIFAC 1969
Splake (brook x lake trout)	4.49	50% mortality of yolk sac in ~6.0 days	Grande et al. 1978
Lake trout (Salvelinus namaycush)	5.5-5.2	Approximate pH when reproduction ceased	Beamish 1976

TABLE III-3. (continued)

Fish species	pH level	Effect and Comments	Reference
Lake trout	4.49	50% mortality of yolk sac in ~1.3 days	Grande et al. 1978
Rainbow trout	4.49	50% mortality of yolk sac fry in ~1.3 days	Grande et al. 1978
Rainbow trout	1^+ age $\bar{x}$ = 6.10	3.5 mo. exposure; 3% mortality	Edwards & Hjeldnes 1977
Rainbow trout	1^+ age $\bar{x}$ = 5.59	3.5 mo. exposure; 4% mortality	Edwards & Hjeldnes 1977
Rainbow trout	1^+ age $\bar{x}$ = 4.98	3.5 mo. exposure; 7% mortality	Edwards & Hjeldnes 1977
Rainbow trout	5.5	Approx. lower limits of tolerance	Berzins 1960 as cited Johansson et al. 1977
Rainbow trout	4.5	LD_{50} to fingerlings in 15 days	Lloyd & Jordan 1964 as cited EIFAC 1969
Rainbow trout	4.2	8 day LD_{50}	Lloyd & Jordan 1964 as cited EIFAC 1969
Brown trout (Salmo trutta)	4.4-5.2	100% mortality of yolk sac fry due to combined low pH and low salt concentration	Grande & Anderson 1979
Brown trout	5.0	Approx. lower limits of tolerance	Berzins 1960 as cited Johansson et al. 1977
Brown trout	4.49	50% mortality of yolk sac fry in ~10.0 days	Grande et al. 1978
Brown trout	1^+ age $\bar{x}$ = 6.20	3.5 mo. exposure; 5% mortality	Edwards & Hjeldnes 1977
Brown trout	1^+ age $\bar{x}$ = 5.50	3.5 mo. exposure; 2% mortality	Edwards & Hjeldnes 1977
Brown trout	1^+ age $\bar{x}$ = 4.77	3.5 mo. exposure; 6% mortality	Edwards & Hjeldnes 1977
Brown trout (Avaa strain)	4.4	66% of eyed eggs survived yolk-sac stage	Johansson et al. 1977
Brown trout (Avaa strain)	4.0	Lethal to 90% of eyed eggs	Johansson et al. 1977
Brown trout (R. Dalalven strain)	4.5	Lethal to 100% of eyed eggs	Johansson et al. 1977
Brown trout (R. Dalalven strain)	5.0	Lethal to 20% of eyed eggs	Johansson et al. 1977

TABLE III-3. (continued)

Fish species	pH level	Effect and Comments	Reference
Brown trout	5.8-6.2	Lethal pH in 2 days; possible CO_2 interaction	Bishai 1960 as cited EIFAC 1969
Brown trout	4.77	50% hatching success	M. Grande as cited EIFAC 1969
Brown trout	<5.0	pH critical to reproduction	Almer et al. 1978 as cited EIFAC 1969
Adult Brook Trout	4.5	5 mo. exposure; 100% mortality	Menendez 1976
Adult Brook Trout	5.08	5 mo. exposure; 31% of eggs viable	Menendez 1976
Brook Trout	5.09	5 mo. exposure; 26% of eggs hatched	Menendez 1976
Brook Trout	5.57	5 mo. exposure; 55% of eggs hatched	Menendez 1976
Brook Trout	6.13	5 mo. exposure; 60% of eggs hatched	Menendez 1976
Brook Trout	6.55	5 mo. exposure; 74% of eggs hatched	Menendez 1976
Brook Trout (Control)	7.04	5 mo. exposure; 82% of eggs hatched	Menendez 1976
Brook trout	4.8	Approx. lower limits of tolerance	Berzins 1960 as cited Johansson et al. 1977
Brook trout	4.5	70% of eyed eggs survived yolk sac stage	Johansson et al. 1977
Brook trout	4.49	50% mortality of yolk sac in ~7.0 days	Grande et al. 1978
Sea trout	5.8-6.2	Lethal pH in 2-day test; Possible CO_2 Interference	Bishai 1960 as cited EIFAC 1969
Perch	4.5 and 5.0	100% mortality of hatched eggs	Runn et al. 1977
Perch	4.4-4.9	pH critical to reproduction	Almer et al. 1978
Yellow perch (*Perca flavescens*)	4.7-4.5	Approx. pH when reproduction ceased	Beamish 1976
Perca flavescens and *Umbra limi*	<4.5	Only species found in Wisconsin Lake Survey	Rahel & Magnuson 1980

TABLE III-3. (continued)

Fish species	pH level	Effect and Comments	Reference
Umbra limi	4.2	Only species present in Wisconsin Lake Survey	Rahel & Magnuson 1980
Walleye (Stizostedion vitreum)	6.0^{+}-5.5	Approx. pH when reproduction ceased	Beamish 1976
Troutperch (Percopsis omiscomaycus)	5.5-5.2	Approx. pH when reproduction ceased	Beamish 1976
Arctic char	1^{+} age $\bar{x}$ = 6.12	3.5 mo. exposure; 0% mortality	Edwards & Hjeldnes 1977
Arctic char	1^{+} age $\bar{x}$ = 5.53	3.5 mo. exposure; 0% mortality	Edwards & Hjeldnes 1977
Arctic char	1^{+} age $\bar{x}$ = 4.84	3.5 mo. exposure; 10% mortality	Edwards & Hjeldnes 1977
Arctic char	5.2	Critical pH for reproduction	Johansson et al. 1977
Arctic char	≤5.2	Critical pH for reproduction	Almer et al. 1978
Char	4.5-5.0	Critical range for hatching	Bua & Snekvik 1972 as cited Hagen & Langeland 1973
Zebra fish (Brachydanio rerio Ham.-Buch)	5.5	20% of eggs hatched	Johansson et al. 1973
Zebra fish (Brachydanio rerio Ham.-Buch)	4.0	4% of eggs hatched	Johansson et al. 1973
White sucker (Catostomus commersoni)	5.2-4.7	Approx. pH when reproduction ceased	Beamish 1976
Fathead minnows	5.2-4.5	Females did not spawn	Beamish 1976
Fathead minnows	5.9	Decreased egg production & hatchability	Beamish 1976
Minnow	≤5.5	Critical pH for reproduction	Almer et al. 1978
Minnow	5.0	Survival time equals 28 days	Carpenter 1927 as cited EIFAC 1969
Minnow	5.2	No effect in 3 days	Carpenter 1927 as cited EIFAC 1969

TABLE III-3. (continued)

Fish species	pH level	Effect and Comments	Reference
Small mouth bass (*Micropterus dolomieui*)	6.0^{+}-5.5	Approx. pH when reproduction ceased	Beamish 1976
Rock bass (*Ambloplites rupestris*)	5.2-4.7	Approx. pH when reproduction ceased	Beamish 1976
Centrarchids	4.6-5.0	Healthy populations found in Wisconsin Lake Survey	Rahel & Magnuson 1980
Lake Chub (*Couesius plumbeus*)	4.7-4.5	Approx. pH when reproduction ceased	Beamish 1976
Cyprinids	>5.0	Only found when pH 5.0	Rahel & Magnuson 1980
Burbot (*Lota lota*)	6.0^{+}-5.5	Approx. pH when reproduction ceased	Beamish 1976
Burbot	6.0	Critical lower level for embryo segmentation	Volodin 1960 as cited EIFAC 1969
Burbot	5.0	Critical lower level for post-embryo development	Volodin 1960 as cited EIFAC 1969
Lake herring (*Coregonus arredii*)	4.7-4.5	Approximate pH when reproduction ceased	Beamish 1976
Brown bullhead (*Ictalurus nebulosus*)	5.2-4.7	Approx. pH when reproduction ceased	Beamish 1976
Roach	4.2	8 day LD_{50}	Lloyd & Jordan 1964 as cited EIFAC 1969
Roach	≤5.5	Critical pH for reproduction	Almer *et al.* 1978
Pike	4.4-4.9	Critical pH for reproduction	Almer *et al.* 1978
Cisco	<5.0	Critical pH for reproduction	Almer *et al.* 1978
Eel	~4.5	Critical pH for reproduction	Almer *et al.* 1978

TABLE III-4. SUMMARY OF THE EFFECT OF pH VALUES ON FISH (From EIFAC 1969).

Range	Effect
3.0 - 3.5	Unlikely that any fish can survive for more than a few hours in this range although some plants and invertebrates can be found at pH values lower than this.
3.5 - 4.0	This range is lethal to salmonids. There is evidence that roach, tench, perch and pike can survive in this range, presumably after a period of acclimation to slightly higher, non-lethal levels, but the lower end of this range may still be lethal for roach.
4.0 - 4.5	Likely to be harmful to salmonids, tench, bream, roach, goldfish and common carp which have not previously been acclimated to low pH values, although the resistance to this pH range increases with the size and age of the fish. Fish can become acclimated to these levels, but of perch, bream, roach and pike, only pike may be able to breed.
4.5 - 5.0	Likely to be harmful to the eggs and fry of salmonids and, in the long term, persistence of these values will be detrimental to such fisheries. Can be harmful to common carp.
5.0 - 6.0	Unlikely to be harmful to any species unless either the concentration of free carbon dioxide is greater than 20 ppm or the water contains iron salts which are precipitated as ferric hydroxide, the toxicity of which is not known.
6.0 - 6.5	Unlikely to be harmful to fish unless free carbon dioxide is present in excess of 100 ppm.
6.5 - 9.0	Harmless to fish, although the toxicity of other poisons may be affected by changes within this range.
9.0 - 9.5	Likely to be harmful to salmonids and perch if present for a considerable length of time.
9.5 - 10.0	Lethal to salmonids over a prolonged period of time, but can be withstood for short periods. May be harmful to development stages of some species.
10.0 - 10.5	Can be withstood by roach and salmonids for short periods but lethal over a prolonged period.
10.5 - 11.0	Rapidly lethal to salmonids. Prolonged exposure to the upper limit of this range is lethal to carp, tench, goldfish and pike.
11.0 - 11.5	Rapidly lethal to all species of fish.

Reference is made to different species on the basis of information known to us; the absence of a reference indicates only that insufficient data exist.

ALUMINUM MOBILIZATION AND TOXICITY

General Reactions of Aluminum

One of the indirect effects of watershed acidification may be the mobilization of aluminum in soils, causing toxic effects on terrestrial organisms and the biota of streams and lakes. Aluminum solubility is pH dependent, and increases with increasing acidity (Figure III-6). Several reports have documented elevated aluminum concentrations in acid lakes and streams in areas known to be impacted by acid inputs (Figure III-7, Davis 1980; Cronan and Schofield 1979; Schofield 1980), and in effluents from lysimeters treated with acid solution (Dickson 1978; Abrahamsen et al. 1976). While aluminum is typically leached from the upper soil horizon of podsol soils by carbonic acid and organic chelation, it is usually deposited in lower horizons. Under the influence of strong acids in precipitation, however, the aluminum may be transported through the soil and leached into lakes and streams (Hall and Likens 1980; Herrmann and Baron 1980). Peak aluminum concentrations generally occur during spring melt of the snowpack (Figure III-8) when large quantities of H+ ions, accumulated over winter, are released and flush aluminum from the soil system (Schofield 1980). As illustrated in Figure III-8, the large majority of impurities are released during the first stages of snowmelt. Seip et al. 1980 note that interactions of meltwater with soil and vegetation are important in determining the amounts of aluminum leached to receiving waters.

Current precipitation in the northeast United States, Norway, and Sweden has pH levels between 3.0 - 4.0 and lower (Likens et al. 1979, Wright et al. 1980, Wright and Dovland 1977). Magistad's (1925) data and more recent data (Baker and Schofield 1980, Clark 1966, Cronan and Schofield 1979, Dalal 1975, Driscoll 1980) show that the pH of incoming precipitation is well within the range of aluminum mobilization resulting in toxic levels (as identified in the laboratory).

The mechanism supplying Al^{3+} is the decomposition of alumino-silicates and gibbsite (Norton 1976, Reuss 1976):

$$Al_2\ Si_2\ O_5\ (OH)_{4x1} + 6H^+ = 2Al^{3+} + 2H_4SiO_2 + H_2O$$

$$Al(OH)_3 + H^+ = Al(OH)_2^+ + H_2O$$

$$Al(OH)_2^+ + H^+ = Al(OH)^{2+} + H_2O$$

$$Al(OH)^{2+} + H^+ = Al^{3+} + H_2O$$

This is likely to occur in watersheds where there are no carbonates to consume H+, and the above reactions become a primary buffering mechanism (Johnson 1979, Kramer 1976). The pH at which this buffering occurs is around 4.5-5.0 as indicated by the Al solubility diagram of Dalal (1975), which shows that $Al(OH)_3$ begins to decline rapidly at pH 5 as Al^{3+} begins to increase. The other soluble Al species, $Al(OH)_2^+$, $Al(OH)^{2+}$ and $Al_6(OH)_{15}^{3+}$, never exceed 10% of total aluminum.

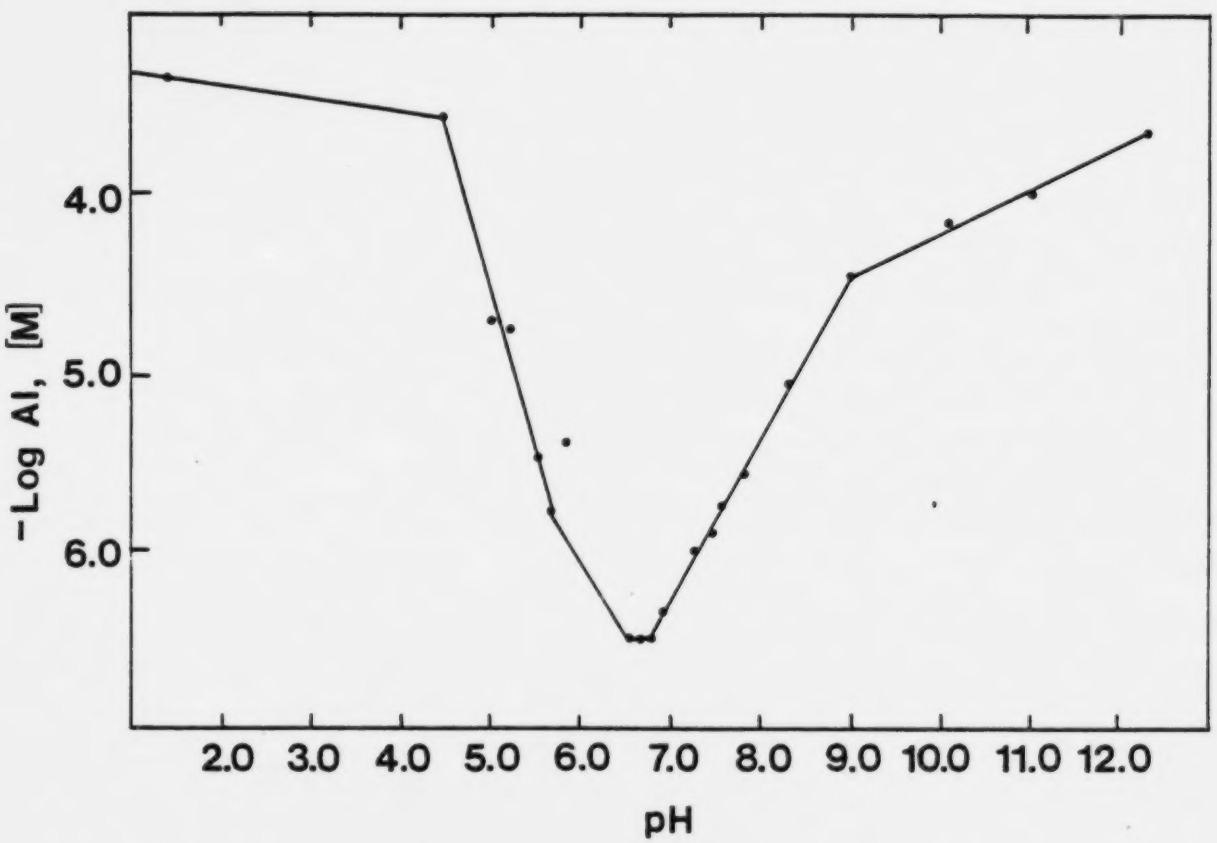

Figure III-6. Solubility of aluminum as affected by pH. Note increasing solubility with increasing acidity. (From Andren et al. 1980.)

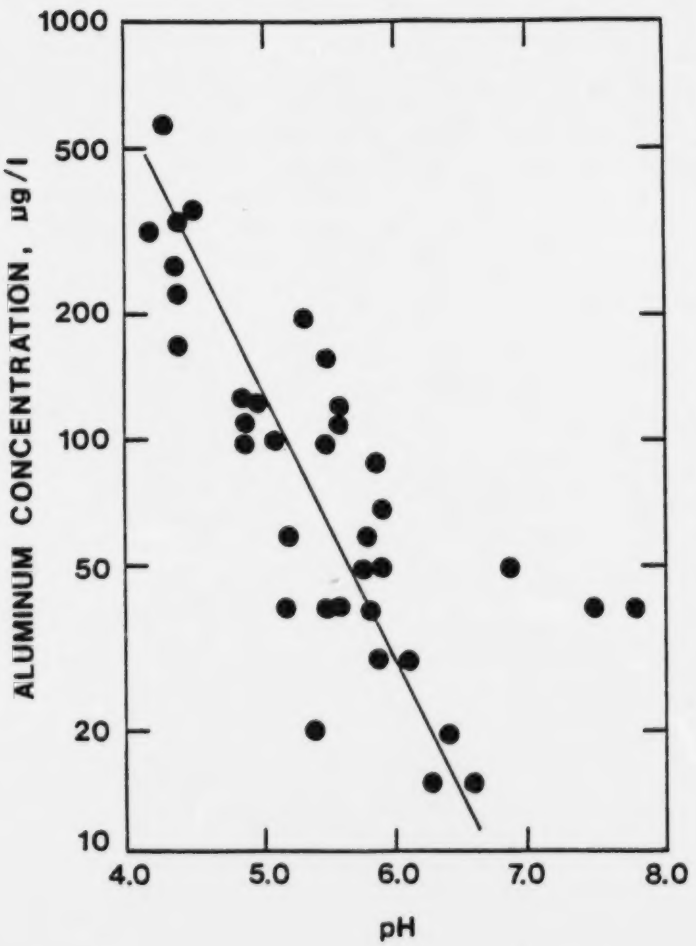

Figure III-7. Aluminum concentrations found in Norwegian and Swedish clear water lakes. (From Davis 1980.)

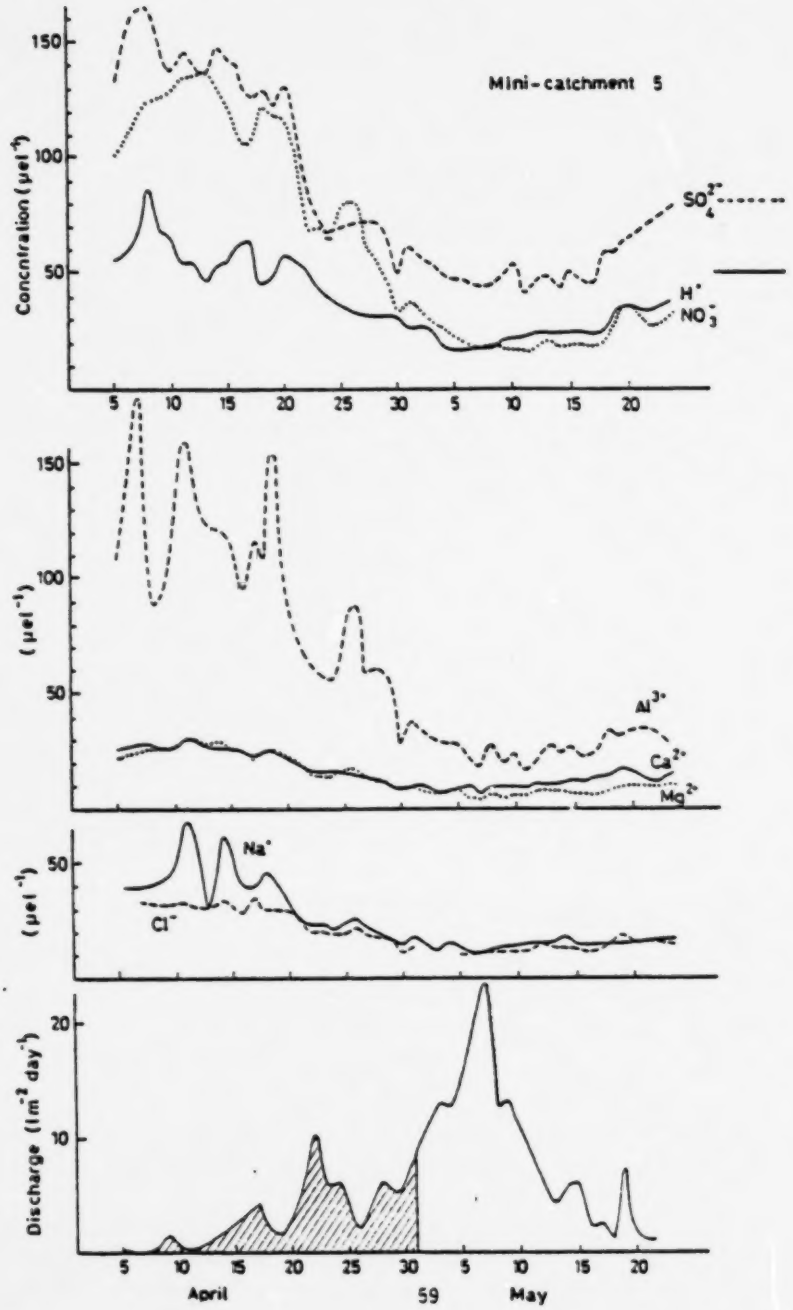

Figure III-8. Nutrient release from snowpack during 1978 spring melt as determined by monitoring runoff from minicatchments in Norway. Note majority of contaminants released simultaneously at initial melt. Shaded area in lower graph corresponds to 30% of the runoff during the period. Dashed and solid lines to right of top figure represent average concentrations of SO_4 and H+, respectively, during summer and autumn 1978. (From Seip et al. 1980.)

In aquatic systems, aluminum forms a variety of complexes with water, hydroxide, fluoride, silicate, organic matter and sulfate (Everhart and Freeman 1973, Driscoll 1980, Baker and Schofield 1980). It is rarely found as the free aluminum ion. According to Johannessen (1980), these complexes act as a buffer in the pH range 4.5-5.0, but above and below these levels buffering cannot be ascribed to aluminum complexes. Henriksen (1980) shows that lakes with pH 4.6 - 4.8 are less acid than expected from a theoretical "titration" curve based on bicarbonate buffering, and that the extra buffering can be explained by aluminum. He postulates that mineral acid addition to lakes will cause them to change from a carbonic acid-bicarbonate buffered system to one buffered by strong acid-aluminum.

In surface waters of the Adirondack Region of New York, Driscoll (1980) found aluminum-organic complexes as the predominant monomeric form (Avg. = 44%), which increased linearly with total organic carbon content. Aluminum-flouride complexes were the most abundant inorganic form (avg. = 29% of the total monomeric Al), with their concentration increasing with decreasing pH, although their formation was generally limited by fluoride concentration. Aluminum sulfate species were of relative unimportance, although they did increase with decreasing pH. Everhart and Freeman (1973) note that the solubility of aluminum is a direct function of pH in the vast majority of natural waters (i.e., under conditions where hydroxide complexes dominate). In acid environments the soluble forms are cationic and polymeric. Overall, pH controls complexation, polymerization, hydrolysis and solubility.

Aluminum also indirectly affects availability of heavy metals and phosphorus. Heavy metal availability increases because humic substances, to which heavy metals are normally bound, are instead complexed and precipitated by aluminum (Davis 1980). Aluminum also precipitates phosphorus, as aluminum phosphate, thus decreasing its availability to aquatic biota.

Terrestrial Effects

The aluminum mobilized by strong acid deposition is of most concern due to its toxic effect on terrestrial and aquatic organisms. Much research on aluminum toxicity has been conducted on crops and legume species (Black 1968, Andrew 1978, Hewitt 1952, Foy *et al*. 1978). From these reports the following statements can be made:

(1) Excess aluminum affects cell division in roots, causing inhibition of root growth leading to stubby and brittle roots. The best indicator of aluminum toxicity in the field is abnormal root development. The tips and lateral roots become thickened and turn brown, and no fine branching roots develop. Al is often found in root cortex cells, being especially concentrated in nuclei. It generally accumulates in roots and is only found in above-ground plant parts of a few plant species. Germinating plants and young seedlings are generally more susceptible than older plants.

(2) Excess aluminum fixes phosphorous in less available forms in the soil and in or on plant roots. Consequently, phosphorous deficiency is often associated with toxic aluminum concentrations and is generally the form of symptom expression in above-ground plant parts. Al has also been shown to interfere with uptake, transport and use of other nutrients (Ca, Mg and K) and water. Thus, Al toxicity can appear as Ca, Mg or K deficiency. In cotton, excess aluminum also decreased uptake of Mn, Fe, Ni and B, some of which must be due to a decreased absorptive surface.

(3) Excess Al also decreases root respiration, interferes with certain enzymes governing the deposition of polysaccharides in cell walls, and increases cell-wall rigidity (by cross-linking pectins). All of these effects of aluminum lead to decreased growth and occur below a pH of 5.0, although effects have been noted at pH 5.5. Andrew (1978) also notes that excess Al is detrimental to nodule initiation in legumes, the efficiency of the nitrogen-fixing symbiosis and plant growth. He also notes that low Al concentrations for short periods of time can increase growth of some plant species.

Various plant species have quite different tolerance levels of Al. Many factors affect tolerance/susceptibility, including: pH around the root zone (tolerant plants can produce a higher pH around root zones); NH_4+ vs. NO_3- nutrition; aluminum exclusion processes; calcium nutrition; phosphorous nutrition; and organic-aluminum complexes. All of these factors are discussed in detail by Foy et al. 1978.

Species known to be sensitive to aluminum include: barley, sugar beet, corn and alfalfa. Decreased growth of barley occurred at < 1 ppm; for corn, 4-17 ppm Al was toxic; and for alfalfa 2.7 ppm was toxic (Black 1968). In experiments with alfalfa grown in nutrient solutions, Munns (1965) found decreases (from controls containing 0.008 ppm Al) in shoot dry weight of 70.3% and 83% at aluminum concentrations of 1.08 ppm and 5.4 ppm, respectively. The first observed symptom was inhibition of root elongation and lateral formation, and plants with high aluminum concentration showed characteristic phosphate deficiency. Tolerant crop species include oats, most brassicas (i.e., caulitlower, narrowstem kale, and swede), rye, rice, soybeans, azaleas, cranberry, and triticale.

For forestry applications, McCormick and Steiner (1978) tested the effect of aluminum on root elongation in six tree genera. A hybrid poplar was most sensitive, with complete inhibition at less than 10 ppm Al. Autumn olive was sensitive at 10-40 ppm, while the other genera (Quercus, Pinus, Alnus, Betula) did not show effects until the concentration was 80-100 ppm. However, concentrations greater than 4 ppm Al are rare in soil solutions (Andrew 1978).

Manganese toxicity also is associated with aluminum toxicity (both occur simultaneously, i.e., under acid conditions). Low concentrations of

1-4 mg/ℓ affect sensitive plants such as lespedeza, soybeans and barley, although corn tolerates >15 mg/ℓ and Deschampsia flexuosa tolerates >60 mg/ℓ (Black 1968). Tolerance is usually attributed to reduced absorption, less translocation of excess Mn to plant tops, and/or greater tolerance to high Mn levels within plant tissues.

Aquatic Effects

Graphs such as those in Figures III-6 to III-8 are important in establishing the relationship between pH and aluminum solubility, but they do not adequately describe peak aluminum mobilization events, nor do they describe the effects of continual input of H+ ions. Peak concentrations in lakes are of utmost importance biologically because they may occur in conjunction with spawning and hatching and are thus most likely to cause adverse effects on fish recruitment (Gjessing et al. 1976). Peak aluminum concentrations also will occur in conjunction with peak hydrogen ion concentrations (Figure III-9) which may increase the overall effect on fish and other biota (see Schofield 1980; and pH and synergisms, this report).

Figure III-9 graphs the relationship between hydrogen ion loading rate and aluminum concentration, and indicates the effects large inputs of hydrogen ions would have on aluminum concentrations in lakes. The points labeled N are from lysimeter studies in which complexation with organic matter increased aluminum solubility. Caution should be used when interpreting the data point D, as the full data set was not available for its calculation. It was assumed that 100 kg H_2SO_4/hectare·year resulted in 1 mg Al/ℓ effluent (see Dickson 1978). Data used in Figure III-9 are from Abrahamsen and Stuanes (unpublished data), Crisman and Brezonik (1980), Dickson (1978), Cronan and Schofield (1979), Likens et al. (1977), and Wright et al. (1978).

The scatter in Figure III-9 indicates that other variables influence Al mobilization. Factors such as soil type (clays retain aluminum), amount of organic matter present, base saturation, cation exchange capacity and absolute aluminum concentration will affect a watershed's response to acid inputs. These factors emphasize the need for more data from various watershed types before conclusions can be made regarding the hydrogen ion loading rate that will result in toxic aluminum concentrations.

Graphs such as Figure III-9 could be used to determine the hydrogen ion input resulting in potentially toxic aluminum concentrations to lake and stream biota, but aluminum toxicity is not that simple, as it is affected by a variety of chemical and biological factors. For example, the points labeled N would suggest that elevated (and hence potentially toxic) aluminum concentrations can occur with relatively small inputs of hydrogen ions. However, these points are a result of increased solubility due to complexation with organic matter, and aluminum is less toxic when complexed to organic matter. Other substances act as aluminum ligands and have the same effect (see previous discussion).

Wright and Snekvik (1978) observed that aluminum caused no deleterious effects at concentrations ranging from 0.05 - 0.3 mg/ℓ, found in 90%

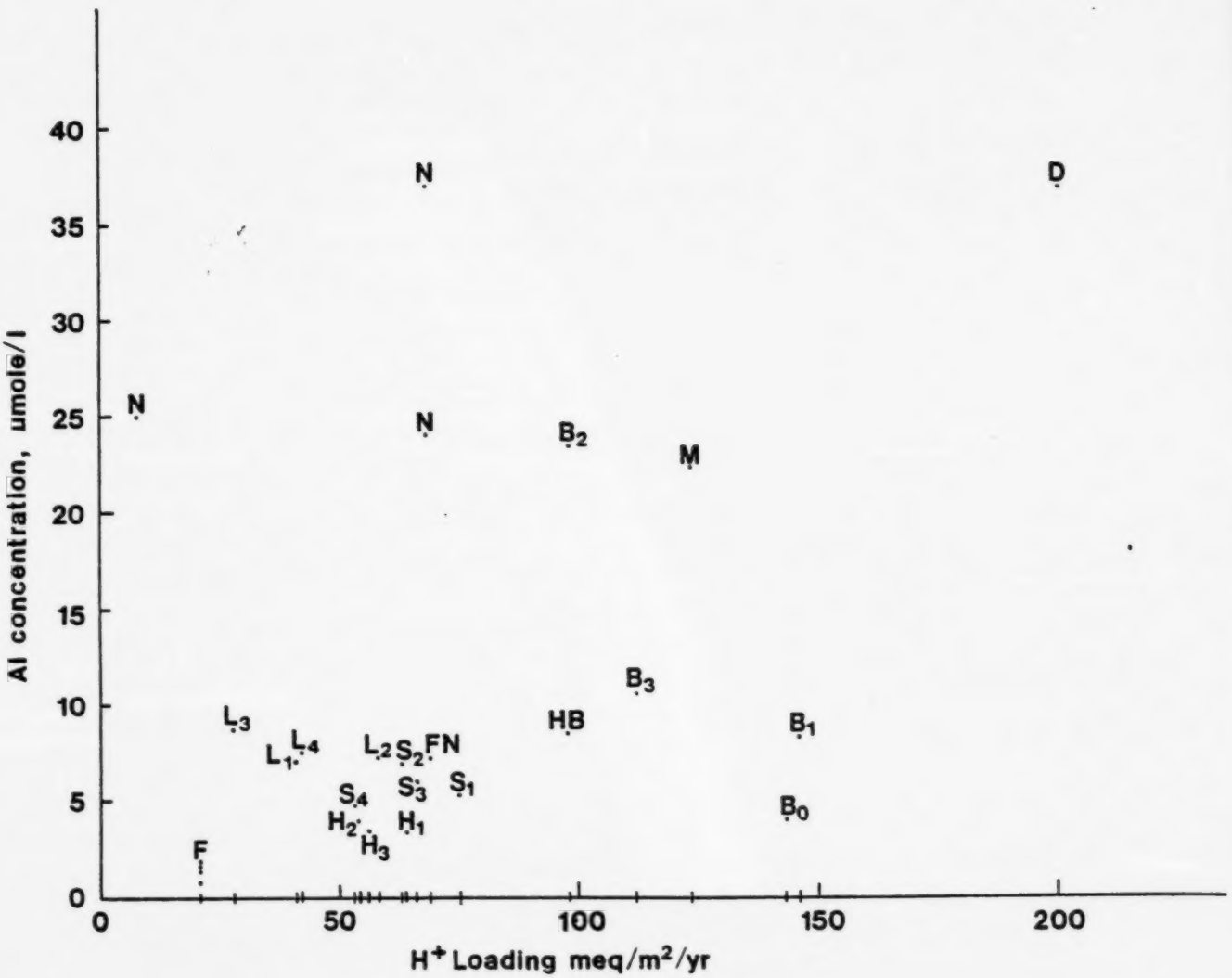

Figure III-9. Relationship between H+ loading rate and observed aluminum concentrations in lysimeter effluent, minicatchments or freshwater lakes. Data from a variety of sources cited in the text.

of the 700 lakes which they surveyed. Their results indicate that fish status was correlated most with Ca and pH, with barren lakes having low pH levels and low Ca concentrations. They note that acid stress to fish is apparently more acute in waters with very low ionic strength. They also found that Ca ameliorates the effects of low pH, with more fish surviving low pH with high Ca concentration than low pH with low Ca concentrations. Nutrient stripping of soils leads to increases in Ca^{2+} concentrations in lakes which could ameliorate the toxic effects of high aluminum and hydrogen ion concentrations.

Some research has been completed on the physiological effects of elevated aluminum concentrations on fish. Muniz and Leivestad (1980) noted a rapid loss of plasma Na and Cl at toxic Al levels, and also large amounts of mucus clogging gills, resulting in hyperventilation and coughing. Venous oxygen tension was decreased in fish with clogged gills. The toxic effect was thus a combination of impaired ion exchange and respiratory distress brought on by mucus clogging of gills. Cronan and Schofield (1979) observed that mortality from acute exposure to aluminum appeared to result from severe necrosis of the gill epithelium.

Estimating peak aluminum concentrations and toxicity to fish with sufficient accuracy is not possible from current data. The relationship between H+ ion input and aluminum concentration graphed in Figure III-9 requires further data for validation. Data on aluminum toxicity (both chronic and shock effects) to various fish species, and under various physical and chemical situations, also are needed. Numerous factors -- pH, ionic strength, calcium concentration, phosphates, organic matter, nitrate, fluoride, sulfate and silicates -- all affect aluminum toxicity. Relationships between these factors and aluminum toxicity need to be identified before "safe" aluminum concentrations can be set. Based on the data presented in Tables III-4 and III-5, highly tentative ranges are proposed as follows: non-toxic concentrations would be below 0.05 mg/ℓ, potentially toxic concentrations would be between 0.05 and 0.3 mg/ℓ, and toxic concentrations would be greater than 0.3 mg/ℓ. These ranges should only be applied to species already tested, trout and salmon, and should not be applied to other fish species.

H+ and Synergisms with Al^{3+}

There has been some work on responses of fish to pH in conjunction with other variables. McLeay et al. (1979) have investigated the toxic effects on salmonid fish of paper pulp effluent as a function of pH. Their results suggest that as pH decreases, mortality increases. They found 50% to 67% mortality at a pH below 7.0, which was the normal pH of the receiving water. Baird et al. (1979) have investigated the toxicity of ammonia as a function of pH.

Aluminum has been found to lower the toxicity of pH to fish, i.e., low pH and some aluminum are more toxic than low pH and no aluminum (Davis 1980, Dickson 1978, and Baker and Schofield 1980). Davis (1980) notes that for brook trout, pH 4.9 was not lethal but that pH 4.9 and 1.0 mg Al/ℓ were toxic to 50% of the population. At pH 4.0, 1.0 mg Al/ℓ was less toxic, although pH 4.0 and 4.4 were toxic by themselves (Figure III-10). Schofield (1980) also found less aluminum toxicity at pH 4.0 than at 4.4

TABLE III-5. SUMMARY OF LITERATURE CONCERNING ALUMINUM TOXICITY TO FISH.

Species	pH	Al	Comments	Reference
Stickleback		0.07 mg/ℓ	Lethal	Dickson 1978
Salmo salar	5.0	0.2 mg/ℓ	Toxic within 6 days	Dickson 1978
Brook trout	4.4-5.9	0.2 mg/ℓ	Toxic response	Cronan & Schofield 1979
Brook trout		0.1-0.3 mg/ℓ	Growth reduction	Cronan & Schofield 1979
Brook trout (*Salvelinus fontinalis* M.)	5.2	0.42 mg/ℓ	28% survival after 2 weeks (mean of 4 replicates)	Driscoll *et al.* 1980
Brook trout	4.4	0.48 mg/ℓ	42% survival after 2 weeks (mean of 4 replicates)	Driscoll *et al.* 1980
Brook trout	4.9	1.0 mg/ℓ	LD_{50}	Davis 1980 (work of Schofield?)
Brown trout (*Salmo trutta*)	4.3, 4.5, 5.0 & 5.3	0.2 mg/ℓ	Mortality occurred	Muniz & Leivestad 1980
Brown trout (*Salmo trutta*)	4.0 & 6.0	0.2 mg/ℓ	No effects	Muniz & Leivestad 1980
Salmon	near 5.0	0.2 mg/ℓ	Very toxic	Grahn 1980
Ciscoe (*Coregonus albula*)	5.0-5.5	max 0.5 mg/ℓ	Large-scale fish kills in 2 lakes	Grahn 1980
-----	(majority <5.0) 4.0-7.0	.05-.3 mg/ℓ	Not deleterious in 700 Norwegian lakes	Wright & Snekvik 1978

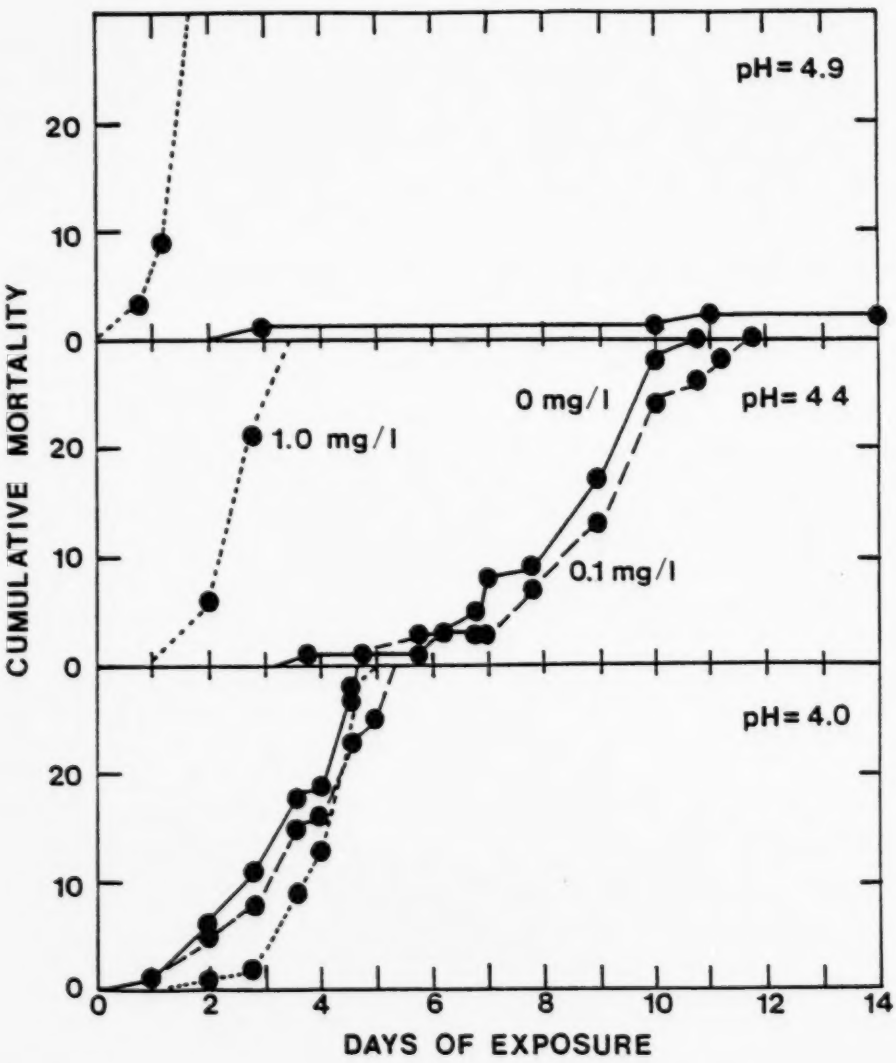

Figure III-10. Effect of altering pH on cumulative mortality of brook trout exposed to three concentrations of aluminum. (From Davis 1980.)

and higher. His results (Table III-6) conclusively show that pH and aluminum do interact in producing fish toxicity. Cronan and Schofield (1979) found that brook trout showed a toxic response to 0.2 mg Al/ℓ (and above) in the pH range of 4.4-5.9. Everhart and Freeman (1973) and Driscoll et al. (1980) also note that aluminum toxicity is pH dependent. Grahn (1980) reports that 0.2 mg Al/ℓ in water near pH 5.0 is very toxic to salmon. He also notes that two fish kills of Ciscoe, Coregonus albula, were associated with low pH (5.0-5.5) and maximum aluminum concentrations of 0.5 mg Al/ℓ. Dickson (1978) relates that 0.2 to 0.6 mg Al/ℓ in association with a low pH (4-5) is toxic to many fish species. Muniz and Leivestad (1980), working with brown trout, Salmo trutta, and aluminum concentrations of 0.2-0.8 mg/ℓ, recorded mortality at pH 4.3, 4.5, 5.0 and 5.3, but no effects at pH 4.0 and 6.0. Maximum toxicity was at pH 5.0 where mortality occurred in 18 hours.

No work has been done on the combined effects of acid pH's and heavy metals, or of aluminum and heavy metals, on terrestrial and aquatic organisms. Synergisms between zinc and copper on fish have been reported by Bandt (1946) and Doudoroff (1952) (both cited by Lloyd 1961), and synergism between nickel and copper on decomposing organisms has been reported by Freedman and Hutchinson (1980). Lloyd noted a possible synergistic effect of zinc and copper sulfates on rainbow trout in soft-water. Czuba and Ormrod (1974) noted synergistic response in lettuce and cress when ozone (O_3) was added in conjunction with Cd or Zn, and similar interactions were noted with SO_2 and Ni or Cu.

HEAVY METAL MOBILIZATION AND TOXICITY

General Soil Reactions

The toxicity of heavy metals to biota was, at one time, assumed to be determined by the total metal concentration in the system (Mancy and Allen 1977). It is now realized that this assumption does not hold, and that toxicity of heavy metals is determined by their particular chemical species. Research must center on determining what species of heavy metals are toxic and at what concentrations; what physical, chemical and biological factors determine the speciation of heavy metals; and the flux rates of heavy metals from the atmosphere to soil to ground water.

Sources of heavy metals fall into two categories: natural and man-made. Natural sources include weathering of mineral bedrock, deposition of marine salts, erosion, volcanism, and forest fires. Man-made sources include industrial and mining wastes, fossil fuel combustion, atomic testing, fertilizers, pesticides, manures, and sewage sludge. To determine transport rates between ecosystem compartments, accurate determinations of the quantity of heavy metals originating from these sources should be calculated, something which has not been done for source inputs to the atmosphere (Goldberg 1975). Goldberg recommends that more research be conducted on the vapor phase of heavy metals, and on vertical and horizontal concentrations of heavy metals, before calculating transport rates from the atmosphere.

Table III-6. TIMES TO 50% MORTALITY FOR FISH IN TRIALS A-F. PERCENT SURVIVAL IS GIVEN IN THOSE TRIALS IN WHICH 50% MORTALITY WAS NOT REACHED AFTER 14 TO 23 DAYS EXPOSURE. NOTE LACK OF EFFECT OF INCREASING ALUMINUM CONCENTRATIONS ON MORTALITY AT pH 4.0. (From Schofield 1980.)

Trial	Nominal pH	Aluminum (mg/ℓ)	Time (days) Replicate A	Replicate B	Replicate C	Mean
A	4.0	0.0	4.1	4.4	5.1	4.5
		0.1	5.4	4.8	5.4	5.2
		0.5	1.9	2.6	4.0	2.8
		1.0	4.8	5.4	4.9	5.0
B	4.4	0.0	9.7	10.0	11.4	10.4
		0.1	11.2	11.2	12.0	11.5
		0.5	1.5	1.8	2.9	2.1
		1.0	3.7	3.3	3.9	3.6
C	4.9	0.0	100%	100%	100%	100%
		0.1	95%	95%	95%	95%
		0.5	2.1	2.1	2.8	2.3
		1.0	1.7	1.6	2.1	1.8
D	4.9	0.25	90% (80%)*	90% (70%)*	90% (75%)*	90% (75%)*
		0.5	3.1	3.1	3.8	3.3
E	5.2	0.0	90%	90%	100%	93%
		0.1	100%	95%	90%	95%
		0.25	65%	70%	55%	63%
		0.5	1.6	1.7	1.5	1.6
F	4.9	0.0	100%	90%	100%	97%
		0.32	95%	75%	100%	90%
		0.65	4.7	4.1	5.3	4.7
		0.63**	11.9	5.4	4.5	7.3

* days survival

** Brook water

Our knowledge of chemistry of metals in soils is incomplete and often speculative (Goldberg 1975). However, numerous factors are known to affect availability, toxicity, and mobility of heavy metals (Ratsch 1974). These factors include (1) relative abundance, (2) form, (3) soil pH, (4) interactions with other elements, (5) physical conditions of the soil, (6) temperature, and (7) soil moisture. Generally, heavy metals do not react to the same conditions in the same manner, so generalizations from one metal to another are not recommended. However, an increase in H^+ ions in precipitation may decrease the ability of the soil system to retain heavy metal ions (Tyler 1972, Abrahamsen and Dollard 1979). In the soil system, heavy metals are found as (1) minerals of soil structures, (2) inorganic precipitates, (3) soluble and insoluble organic complexes or chelates, and (6) absorbed ions on charged surfaces of clays, precipitates and organic matter (Goldberg 1975).

Heavy metals tend to accumulate in soils (VanHook et al. 1977, and Tyler 1972) and generally do so by exchange reactions, whereby organic matter of the soil complex binds heavy metals forming stable complexes (Abrahamsen and Dollard 1979, Tyler 1972). Accumulation occurs in/on dead organic matter, litter and humus, with concentrations increasing with age and extent of decomposition (Tyler 1972, Van Hook et al. 1977). Humic and fulvic acids are believed to play a prominent role in accumulation and cycling of trace metals in soils and sediments (Nriagu and Coker 1980).

In aquatic systems, heavy-metal speciation is subject to change by biological, physical and chemical factors (Wollast et al. 1975, Elder 1978, Chakoumakos et al. 1979). These factors include: pH, water hardness, alkalinity, organic matter content, nutrient content, and oxidation-reduction potential (Goldberg 1975, Gambrell et al. 1980, Elder 1978, Chakoumakos et al. 1979). In freshwater systems, heavy metals can exist in three forms: readily available (biologically), potentially available, and essentially unavailable. Processes affecting the availability of toxic metals include: (1) precipitation as insoluble sulfides under highly reduced conditions; (2) formation of metal oxides and hydroxides of less solubility; (3) absorption to colloidal hydrous oxides of iron and manganese (primarily under aerobic, neutral or alkaline conditions); and (4) complex formation with soluble and insoluble organic matter under all conditions of pH and oxidation potential (Gambrell et al. 1980). According to Allen et al. (1980), most studies suggest that free metal ions are the most toxic form, and that the stronger the complex, the lower the toxicity.

The following summaries illustrate how various factors interact with specific heavy metals.

Mercury: Increased levels of soluble mercury were found by Gambrel et al. (1980) in moderately acid, reduced conditions (pH 5.0, -150mV) and weakly alkaline, oxidized conditions (pH 8.0, +500mV). Wollast et al. (1975) note that mercury is highly soluble only in well-oxygenated water, and that under moderately oxidizing conditions the predominant species of mercury is undissociated. They report that under more reducing conditions extremely insoluble cinnabar (HgS) precipitates, but that under very reducing conditions mercury may increase in solubility. Dissolved mineral mercury can

be present as $Hg(OH)_2$ in the aerobic zone and in elemental form (or as organically complexed oxidized species) in oxidizing conditions. Mercury also exists in several organic forms, e.g., methyl mercury, which are products of bacterial activity.

Zinc: In freshwaters zinc has been found to occur in both ionic and colloidal inorganic forms (Allen et al. 1980). pH was found to affect the levels of total dissolved and exchangeable zinc, with highest concentrations found at the most acid pH employed, 5.0 (Gambrell et al. 1980). At that pH it is most likely to be found in the free cationic form. Soluble zinc decreases under reducing conditions.

Lead and Cadmium: Florence (1977), as cited in Allen et al. (1980), has shown that in freshwaters, lead is present to an equal degree in both inorganic and organic forms, while cadmium is present as the free metal ion. Gambrell et al. (1980) found little dissolved lead at any pH-redox combination (pH 5.0 to 8.0; redox -150mV to +500 mV). They also found that exchangeable lead (readily available) was more influenced by pH than redox potential (higher concentrations found at pH 5.0 than 6.5 and 8.0), whereas reducible lead (metal oxides and hydroxides) was more influenced by oxidation strength than pH (higher levels found at +500 mV than -150, +50 or +250mV).

Copper: In fresh waters copper is predominantly associated with organic colloidal matter (Allen et al. 1980), and is often bound to humic acids (Nriagu and Coker 1980). Elder (1978) studied copper speciation in two alkaline freshwater lakes in California, pH 7.7 - 9.0. Based on the copper concentration and pH of a lake, he constructed a model of expected speciation of copper in an aqueous solution. Below pH 5, all of the copper is free Cu^{2+}. He also discusses the fact that all copper in the lake eventually reaches the sediments. Under anoxic conditions, there is a low redox potential and a release of hydrogen sulfide from sediments. Copper complexes with sulfur to form CuS, which permanently sequesters copper in sediments.

Terrestrial Effects

As indicated above, the soil system is capable of accumulating heavy metals in potentially toxic concentrations, depending on the level of inputs and mobilization reactions. The most common symptoms of heavy metal toxicity on crops and other plants are chlorosis and stunting. Chlorosis is generally caused by direct or indirect heavy metal interactions with foliar Fe (Foy et al. 1978). Oats have often been used as indicator plants for Ni toxicity because of their unique chlorotic and necrotic reaction. Stunting can be caused by specific metal toxicity, antagonism with other nutrients, or inhibition of root penetration. Toxicity is first expressed in root tips, and lateral root development can be severely restricted. If root development is altered, this will also affect normal nutrient uptake, which could lead to decreased productivity.

Aquatic Effects

Once in the aquatic environment, heavy-metal chemistry becomes very complex, as many factors interact to determine the chemical species found. Because of this, extrapolating experimental results from one aquatic system to another can lead to error; i.e., "safe" concentrations in one system may not be "safe" in another. Even so, water quality criteria are set, with a single standard for all freshwater systems. The following brief review of the literature shows the variability in heavy metal toxicity, but also gives an idea of the concentrations which are "safe" to freshwater fish. Unfortunately, most of the experiments were conducted under neutral to alkaline conditions and thus do not reflect toxicities under acid conditions.

Copper: Factors known to affect copper toxicity include pH, hardness, alkalinity, and inorganic and organic complexes. Chakoumakos et al. (1979) studied the effects of alkalinity, water hardness, and pH on copper toxicity to Cutthroat trout. There was an inverse relationship between acute toxicity and water hardness and alkalinity. Copper was more toxic in soft water than hard water. Toxic species of copper were Cu^{2+}, $CuOH^{+}$, $Cu(HO)_2^{0}$ and $Cu(OH_2)^{2+}$ while $CuHCO_3^{+}$, $CuCO_3^{0}$ and $Cu(CO_3)_2^{2-}$ were not toxic. Lett et al. (1976) studied copper toxicity on rainbow trout. They determined a 96-h LC_{50} of 0.25-0.68 mg Cu/ℓ for hard water (365 mg $CaCO_3$/ℓ) and pH 7.8-8.2. Beamish (1976) notes that 17 µg Cu/ℓ did not affect survival, growth, or reproduction of adult rainbow trout in soft water. Sauter et al. (1976) recommend that the safe concentration proposed in 1973 by the National Academy of Sciences (not to exceed 0.1 of the 96 h-LC_{50} for the species of interest) should be changed, based on the results of their study.

Zinc: Spehar (1976) determined a 96-h LC_{50} of 1500 µg Zn/ℓ to juvenile (4 to 5-week-old) flagfish and an estimated MATC (maximum acceptable toxicant concentration) of 26-51 µg/ℓ in Lake Superior water. He found survival of larvae and growth of females to be the most sensitive measures of toxicity. Lloyd (1960) notes that rainbow trout are capable of acclimation to lethal concentrations of zinc if they are first exposed to sublethal concentrations. Ball (1967a) studied zinc toxicity to four freshwater species and found five-day LC_{50}'s for each: rainbow trout 4.6 mg/ℓ; bream 14.3 mg/ℓ; perch 16.0 mg/ℓ; and roach (two strains) 17.3 mg/ℓ. Cairns and Scheier (1957) as cited by Mount (1966) found that bluegills were killed in soft water by 1.93-3.78 ppm Zn, whereas in hard water the values were 10.13-12.15 ppm.

Cadmium: For juvenile (4 to 5-week-old) flagfish in Lake Superior water, a concentration of 2500 µg Cu/ℓ was toxic to 50% of the population in 96 hours (Spehar 1976). Spehar determined an MATC of 4.1-8.1 µg Cu/ℓ with the latter concentration inhibiting reproduction on a chronic basis. Spawning and embryo production were the most sensitive measures of cadmium effect. Ball (1967b) estimated a 7-day LC_{50} of 0.4 mg Cd/ℓ for rainbow trout, but he cites Schweiger's (1957) 4 mg Cd/ℓ as lethal to rainbow trout in seven days, and 3 mg/ℓ as a safe dose. Sauter et al. (1976) conclude that

the National Academy of Sciences' recommended safe concentration of 0.004 mg Cd/ℓ for water with hardness 100 mg $CaCO_3$/ℓ is barely adequate; and that for water with hardness 100 mg $CaCO_3$/ℓ, a recommended safe concentration of 0.03 mg Cd/ℓ is totally inadequate to protect aquatic life.

Lead: Davies and Everhart (1973) found the following toxicities for rainbow trout: in hard water (243 µg $CaCO_3$/ℓ) 96-h LC_{50} for total lead was 471 mg/ℓ, but for dissolved lead it was 1.38 mg/ℓ; in soft water (26.4 mg $CaCO_3$/ℓ) the 96-h LC_{50} for dissolved lead was 140 µg/ℓ. They estimated MATC's for lead: hard water and total lead (0.12-0.36 mg/ℓ); hard water and dissolved lead (0.018 to 0.032 mg/ℓ); and for softwater dissolved or total lead (6.0-11.9 mg/ℓ). Pickering and Henderson (1965) as cited by Davies and Everhart (1973) working with hard water (300-360 mg $CaCO_3$/ℓ) and soft water (18-20 mg/ℓ), determined the following 96-h LC_{50}'s for lead: fathead minnows in soft water - 5.58 mg/ℓ; in hard water - 482 mg/ℓ, for bluegills in soft water - 25.8 mg/ℓ, in hard water - 442 mg/ℓ. Sauter et al. (1976) conclude that the National Academy of Sciences' recommended maximum allowable concentration of 0.03 µg Pb/ℓ appears adequate to protect most fish species.

Heavy-metal toxicity in soils and freshwater ecosystems is very complex, with numerous factors (physical, chemical and biological) interacting in complex ways to determine the chemical speciation, and hence mobility and toxicity, of heavy metals. All heavy metals do not react in the same manner to the same set of conditions, so extrapolation from one heavy metal to another is not reliable. More research is needed to determine the residence times of heavy metals in various ecosystem components, and to find the extent to which heavy metals are recycled in terrestrial ecosystems. Finally, the chemical species of heavy metals which are toxic, and those that are not, need to be determined. In determining toxicities, experiments should be conducted using soil and organisms from the terrestrial site in question.

SECTION IV

METHODOLOGIES FOR QUANTIFYING THE SENSITIVITY OF TERRESTRIAL AND AQUATIC AREAS

Orie Loucks, Richard Miller, Roland Usher and William Swanson

The exposure of forests to oxidants and the addition of acidic pollutants to a lake/watershed ecosystem both alter the producing system, but in very different (although potentially interactive) ways. The oxidant effects (mainly O_3) on forest growth have been reviewed by the authors in the recently completed ORBES study (Loucks et al. 1980) and in a recent symposium (Miller 1980). No additional review will be added here. The aggregate effect of the acidic inputs to the ecosystem, however, may be thought of as a large-scale titration (Henriksen 1980), but it is a complex, uneven process only superficially similar to a laboratory titration. Gorham and McFee (1980) and Last et al. (1980) discuss the variables involved and note that the hydrogen ions deposited with precipitation (or generated by other components of precipitation) may have several fates in the lake/watershed system, as reviewed in the previous section.

Various consequences follow. First, the mobilization of elements by cation displacement can cause a long-term loss of soil fertility and lower productivity. Even if there is an initial fertilization effect from the added nitrogen in precipitation, continued acid input may result in future nutrient limitation through the loss of essential cations. Secondly, the mobilization of aluminum and heavy metals by cation displacement and weathering can result in toxic effects for both the aquatic and terrestrial components of the system. Finally, unneutralized H+ may itself be toxic and a stress to the system.

The combined effects of these above-ground and below-ground processes, as they influence the more highly integrative measures of response, are discussed in the following sections from the viewpoint of data needs in measuring forest, lake or watershed sensitivity.

MEASURES OF SENSITIVITY TO FOREST PRODUCTIVITY RESPONSES

The yields of forests usually are expressed as wood volumes, and growth rates are expressed as cubic feet (or meters) per unit area, per year. These volumes are affected by the annual diameter growth rate, but, since total volume is greatly influenced by the height of the cone (and diameter increment is intercorrelated with annual height growth), height growth is a very frequent measure of forest productivity (Forbes 1955).

Oxidants and acid rain, however, are relatively recent incursions on forest processes (Miller 1980), and, therefore, most studies have reported changes in foliate condition and diameter growth of mature trees -- not in young, developing stands. Many other factors, including insects and disease problems, interact with the mature tree, however, suggesting that the height response of younger stands would have more general application.

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Various measures of soil texture and soil nutrient status have been correlated with forest growth rates, and (as reviewed in the previous section) these suggest various measurements linking a forest response to the agents of chemical alteration in the soil, i.e., acidic deposition. However, height and diameter growth of the forest represents an "integrator" of soil conditions, including, potentially, the alteration of nutrient status due to cation stripping or aluminum toxicity. These growth measures, however, are also the "integrative" measures that would respond to toxic gaseous pollutant inputs to the forest canopy -- SO_2 as well as O_3.

Of the height and diameter measures used in forestry, the most generalizable is Site Index, a basic measure expressing rate of height growth. The Site Index (SI) concept has been accepted routinely in forestry as the best measure of current or potential forest productivity because rates of height growth are readily converted to cubic volumes of wood. The SI is most commonly expressed as the average height of dominant and co-dominant trees at the age of 50 years. It is used in forestry to express the rate of productivity for a single species in a specified site, or mapped aggregate of sites. Although SI usually is specified by height and age measurements, it can be estimated indirectly by using soil and topographical factors (Hannah 1968, Mader 1963), height and age (Spurr 1952), available nutrients (Ellerbe and Smith 1963, Gordon 1964, Heilman 1968) and available soil water and nutrients (Fralish and Loucks 1975, Mogren and Dolph 1972).

A review of the literature since 1960 shows that the primary variables associated with SI are the available soil water and topography (Mogren and Dolph 1972, Fralish and Loucks 1975, Hannah 1968). The importance of soil type and structure has been discussed (Hannah 1968, Richards and Stone 1964, Linnartz 1963) and, although the literature appears to be divided (Broadfoot 1969, Hannah 1968), one of the most important underlying factors affected by site quality is the rooting pattern of the trees under investigation. This directly correlates with the available soil water and nutrients in solution, which, in turn, are a function of precipitation and water use.

To determine site index directly the height and age of the dominant and co-dominant trees must be known (Curtis et al. 1974). Plotting height versus age (Figure IV-1) of dominant stems in a series of stands results in a collection of points which can be broken down into a family of curves, each representing a separate site class. Thus, simply stated, the site index is the height of the stand projected through time, either forward or backward. This projection can only be accomplished through the series of harmonic curves illustrated in Figure IV-1. In the United States, 50 and 100 years have been chosen as reference points for the expression of site index.

There have been a number of investigations relating the role of nutrients to the SI (Gordon 1964, Heilman 1968). Mogren and Dolph (1972) observed the influence of pH on the SI and concluded that there was no effect. It should be noted that they did not report any pH values in the report. A more recent preliminary literature search (1965 to date) has shown that chronic and acute pH changes as they affect the SI have not been investigated.

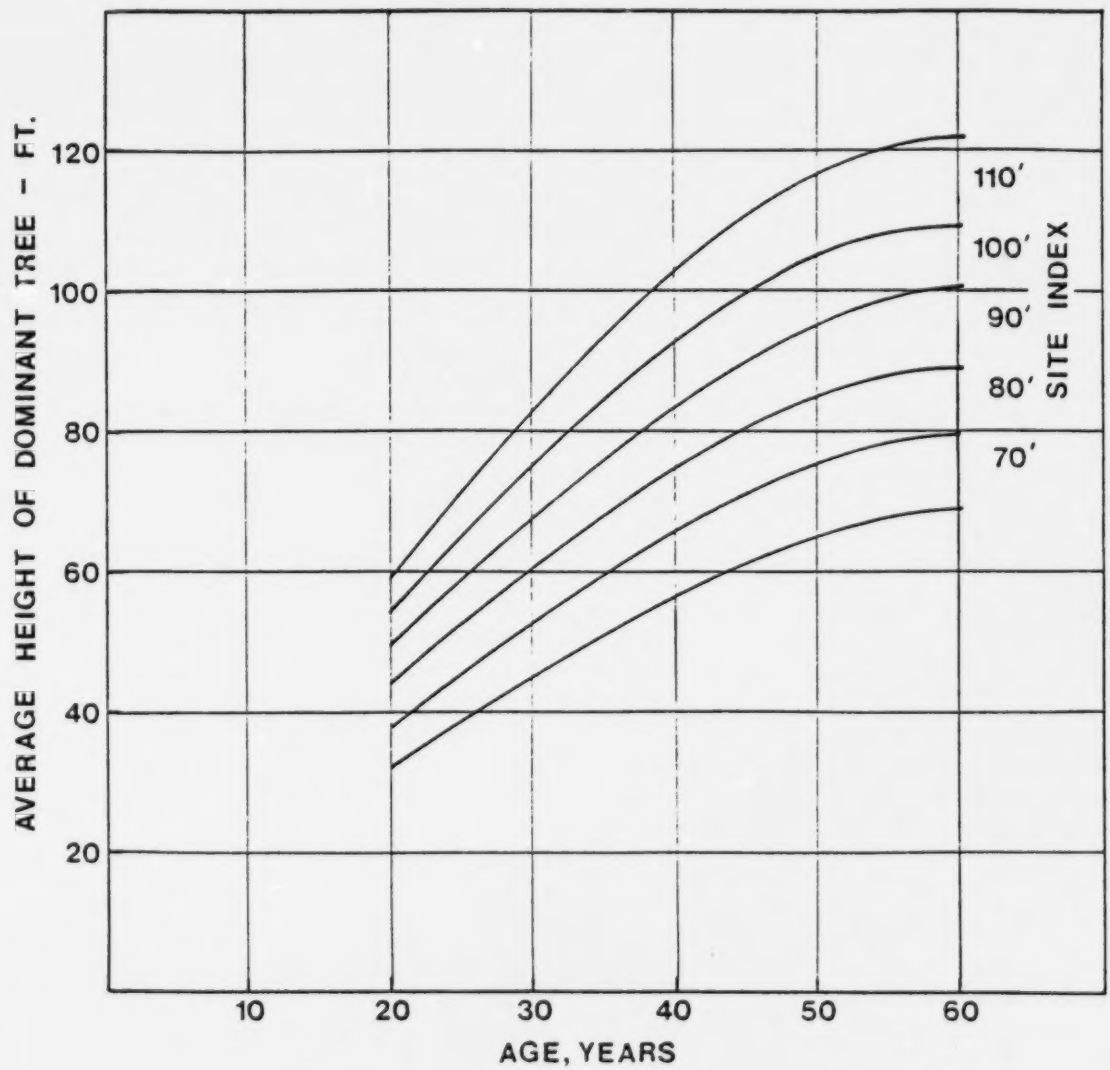

Figure IV-1. Site index classes determined by plotting age against average height of dominant tree.

Use of the forest site index as a measure of terrestrial ecosystem stress from acidic deposition is an attempt to integrate the effects of nutrient additions (such as N and S), nutrient losses such as Ca, Mg, K and Na, and the toxic effects of aluminum, H+ and heavy metals (Drablos and Tollan 1980).

There are several liabilities to this approach. The first relates to age classes. The site index can only be applied if the average site quality is the same for each age class. This liability is important in managed forest sites (Spurr 1956) due to many practices that are used to increase yields. A second liability stems from the assumption that the shape of the height/age curve is consistent between sites. This generalization is capable of reliable results; however, it does not hold for all soils (Figure IV-2). A third liability, related to the second, is that site differences are apparent at an early age. In other words, the harmonized curves that predict a taller tree at 50 years assume that this tree has always been taller. To alleviate the influences of these liabilities, the standard site index curve should be based on specific soil types and field measurements of species growth on that site.

The site index is typically used in forest management to determine harvest schedules for even-aged, monocultural stands. This relationship severely limits the uses of the site index from an ecological viewpoint. A mixed-species and uneven-aged stand presents many fundamental problems in determining a site index curve. To alleviate these problems, Curtis and Post (1964) have proposed a "Composite Site Index" to express site quality in mixed hardwood stands. Their concept uses the measured site index of each species, each of which is converted by means of equations (Curtis and Post 1962) to an estimated maple site index. All the estimated maple site indices are added to the measured maple site index and then averaged, which results in the composite site index. This provides a more reliable measure of site quality for an unmanaged, even-aged site. Curtis et al. (1974) have presented a detailed review article on the importance of the site index and how best to interpret the series of curves obtained.

The effects of acid precipitation on a watershed/lake system are many and intricately balanced, especially in a mature system. As has been outlined above, the site index may be an appropriate tool to measure the effects on, or changes in, site quality due to acid precipitation. Use of the site index as an integrator of acid deposition effects (via nutrient stripping and Al toxicity) has the advantage of being readily convertible to economic terms for cost-benefit analysis. At this time, however, there is not enough data to validate its use.

MEASURES OF AQUATIC ECOSYSTEM SENSITIVITY

At the present time there is no single, fully validated methodology for estimating the sensitivity of aquatic systems to acid deposition. Thus, measures of aquatic sensitivity to acid inputs should be thought of as hypotheses constructed with a reasonable amount of quantitative inputs, but evaluation should not be based on any one model or measurement procedure. All of the methodologies given below are limited in scope and/or

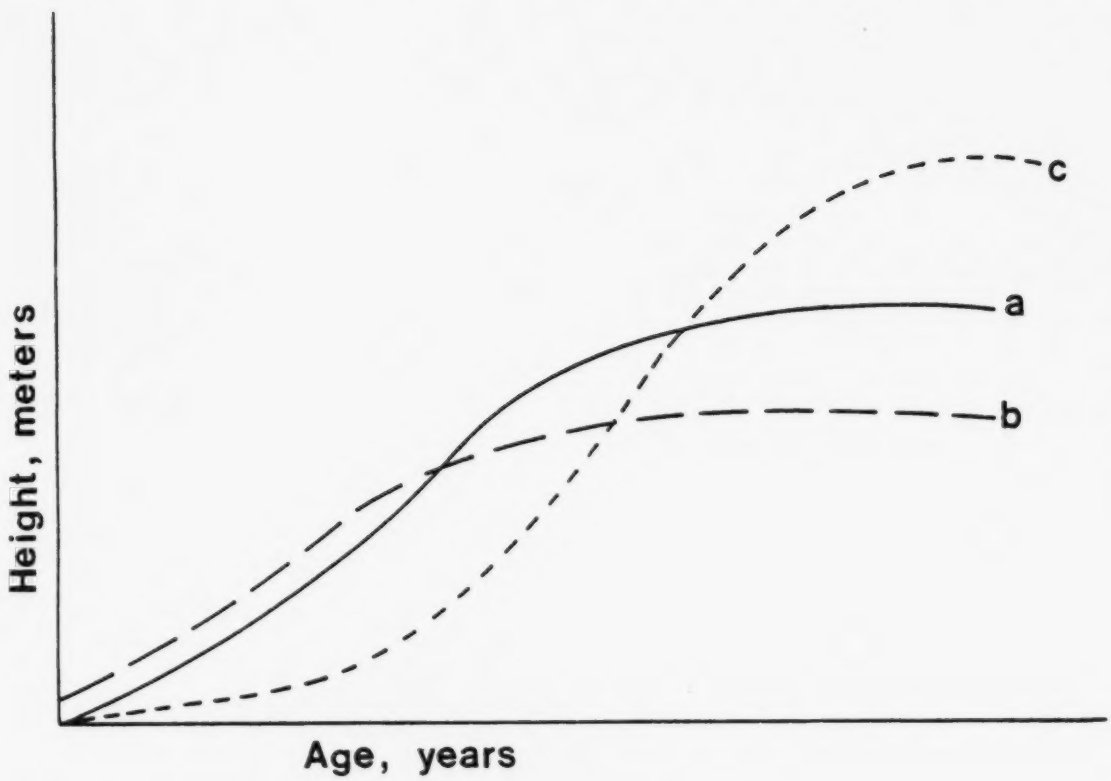

Figure IV-2. Theoretical height/age curves for three soils: (1) homogeneous soil, (b) shallow soil, (c) poor surface soil with richer lower horizons (redrawn from Spurr 1964).

availability of data, but taken together they present a comprehensive view of our ability to quantify current resource status and, therefore, some prediction of prospective future change.

Predicting Toxicity to Aquatic Organisms

Determining toxic effects of acid precipitation on aquatic organisms requires that standard methods be identified. Such standard methods exist for determining general toxicity to aquatic organisms, and can be applied to the toxicity of acid precipitation. Bioassay tests, conducted under natural conditions and employing standard procedures, are a recommended method.

Toxicity is determined by dosage - the amount (in relation to body weight or growth medium) of toxicant and the frequency and duration of exposure (Gough et al. 1979). The term is used by a wide variety of professionals, including doctors, pharmacists, microbiologists, and regulatory personnel.

Although chemical analysis and standardized tables would be the easiest way to determine toxicities, they have not proven to be feasible for many reasons: (1) the specific organism in question often has not been tested; (2) different bodies of water have different characteristics which greatly affect toxicity of many substances, and (3) there are differences in temperature, fish size, seasonal tolerance of various fish species, testing procedures, physiology, previous history, nutritional state, and certain laboratory conditions which may have affected the results (Katz 1971; American Public Health Association 1965).

It is now recognized that bioassay with organisms of the indigenous population under natural conditions is the most satisfactory means of determining toxicities of substances (Peltier 1978, Geckler et al. 1976, American Public Health Association 1965, Katz 1971). Ideally, the tests should employ a range of concentrations of toxicants, and should be conducted at different seasons of the year to reflect differing water quality, which has been shown to greatly affect the toxicity of substances, especially heavy metals (Geckler et al. 1976, U.S. EPA 1976, Katz 1971).

The earliest recommendations for standard methods were published by Hart et al. (1945) and Doudoroff et al. (1951), and have largely been adopted by the American Public Health Association (1965). Other documents are available which outline standard procedures for determining toxicity of elements to aquatic organisms: U.S. EPA (1972); Peltier (1978); and The Committee on Methods for Toxicity Tests with Aquatic Organisms (1975). Numerous review articles have been published on the measurement of pollutant toxicity to fish (Sprague 1969, 1970 and 1971; Herbert 1965; Edwards and Brown 1967; Alderdice 1967; Burdick 1967; and Warner 1967).

Acute toxicity to fish is most frequently measured by the concentration of toxicant that is lethal to 50% of the population within a specified time period (usually 96 hours). Various terms are used, e.g., Median Lethal Dose (LD_{50}), Median Lethal Concentration (LC_{50}), Median Tolerance Limit (TLm), Median Effective Dose (ED_{50}), and Median Effective Concentra-

tion (EC_{50}), although LC_{50} and EC_{50} are preferred. The latter also can refer to lethal or sublethal responses. When used to determine sublethal responses, EC_{50} is defined as the concentration causing an "adverse effect" in 50 percent of the population within a specified time period, where "adverse effect" is generally defined as immobilization.

Three procedures for determining LC_{50}'s and EC_{50}'s are discussed by Sprague (1969) from which the following is largely taken. For all three, tests are conducted using a series of concentrations of the toxicant, with mortality being recorded at various times. The results are plotted on log-probability paper, as shown in Figure IV-3 (from Sprague 1969). From such a graph, one can determine median survival times (when acute mortality ceases), and the presence of differing modes of action. Changes in slope or grouping of lines are clues to differing modes of action. The next step in determining the LC_{50} is to plot all the median lethal times (obtained from graphs similar to Figure IV-1) against concentration to find a lethal threshold concentration.

A second procedure for determining LC_{50}'s is described in Standard Methods (American Public Health Association 1965) and by the Doudoroff Committee (1951). It yields LC_{50}'s for specified time periods, usually 1, 2 or 4 days. For each fixed time, percentage mortalities are plotted against test concentrations, and the concentration lethal to 50% of the population is then estimated by interpolation. Sprague (1969) suggests that more frequent observations be made and that investigators should construct time-concentration toxicity curves as described above.

No reports specifically outline standard procedures for determining chronic toxicity. This underscores the fact that chronic toxicity tests have only recently gained the interest of toxicologists (Gough et al. 1979). Long-term studies using a wide range of concentrations of a particular toxicant on large numbers of aquatic organisms, which determine the overall community response, are needed by regulatory agencies (U.S. EPA 1976). Geckler et al. (1976) suggest that tests other than those on survival, growth, and reproduction be conducted; specifically, that tests based on behavioral responses may better predict effects of toxicants on natural systems. They concluded from their tests with copper, conducted over a 33-month period, that organisms avoided the highest concentrations of copper. Results of chronic tests can be expressed either in terms of the lifetime of one organism or the time span of more than one generation. Chronic effects often influence the species population and not just individuals.

Sprague (1970, 1971) and Mount and Stephan (1967) discuss various methods of determining sublethal or "safe" concentrations, including the use of toxic units and application factors. The latter procedure involves taking the LC_{50} and applying some factor (generally .1) to determine the "safe" concentration.

In conclusion, the following recommendations can be made for measuring effects of acid precipitation on lake/watershed ecosystems:

(1) That additional standard bioassay tests determining LC_{50}'s and EC_{50}'s be used when toxicity tests are conducted;

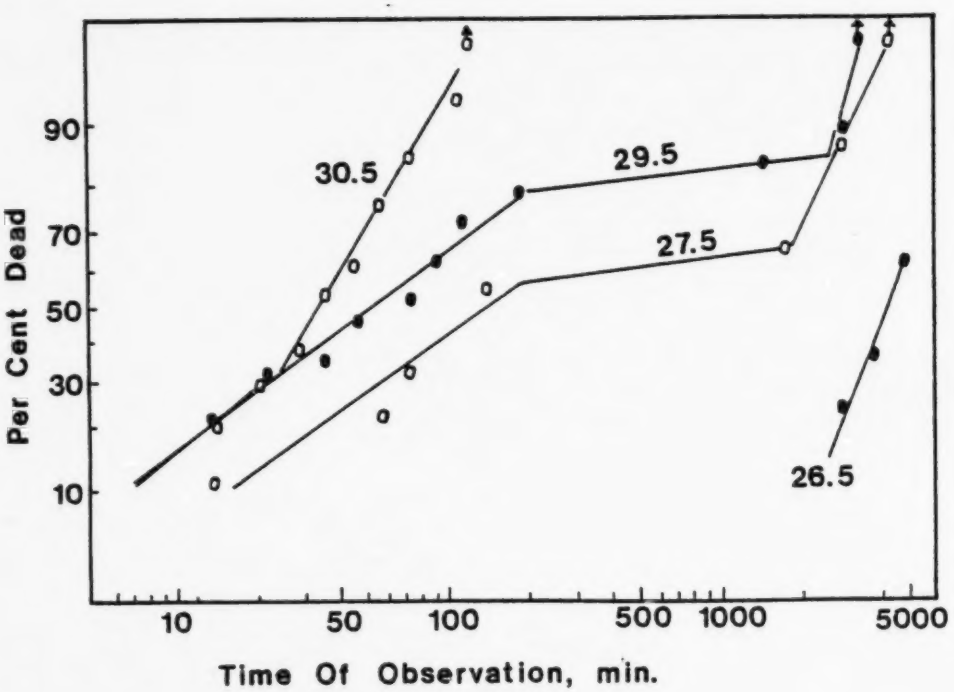

Figure IV-3. Results of a mortality test at various temperatures plotted on logarithmic-probit paper. The results indicate two modes of lethal action at 27.5°C. (From Sprague 1969.)

(2) That the results of these toxicity tests be presented as a range, indicating the variable effect that water quality can have on the toxicity of many substances, particularly heavy metals;

(3) That extrapolation of results of toxicity tests from one body of water to another, and from one species to another, be avoided except where absolutely necessary. It should be noted that extreme variability can exist from one aquatic system to another, from one species to another, and from one season of the year to another.

The Calcite Saturation Index (CSI)

Kramer (1976) has summarized the relationship between pH and alkalinity in the calcite saturation index (CSI) which expresses the relative saturation of water with $CaCO_3$.

$$CSI = p(Ca^{2+}) + p(Alk) - p(H+) + pK,$$

where $p(X) = -\log_{10}X$, $pK = 2$, (Ca^{2+}) is given as mol/ℓ and (Alk) and (H+) are given as eq/ℓ. When CSI < 1, the lake is nearly saturated with $CaCO_3$ and not susceptible to acidification. Increasing CSI indicates increasing susceptibility, and, at CSI > 4, the lake is very likely to be affected by acid (Glass and Loucks 1980).

The CSI has been used to classify lakes sensitive to acidification (Glass and Loucks 1980, and others) and is a relatively simple way to account for lake buffering capacity. However, it is not comprehensive enough to be used as a sensitivity index as defined earlier for watersheds because buffering capacity is only one aspect of lake/watershed sensitivity. It is necessary to account explicitly for other possible consequences of the acid input, including the mobilization of aluminum and the loss of soil fertility by cation stripping. Moreover, the CSI reflects only present conditions and does not relate past or future changes to loading rates. There is no indication in CSI of how a lake came to have a particular value, or of any explicit relationship between the CSI and acidic inputs.

The Dickson Relation

One way to summarize the relationship between lake pH and atmospheric loading of acidic pollutants is to plot lake pH in relation to measured local sulfate loadings, as attributed to Dickson (Almer et al. 1978), Figure IV-4. Various combinations of watershed characteristics are reflected in the family of curves connecting the different sets of lake data. A larger number of curves may be envisioned, each representing lake/watershed systems of comparable sensitivities as they apparently respond to increases in atmospheric acid inputs. The curves are superficially similar to titration curves, as might be expected, and each shows buffering at high pH, then a rapid drop (as this buffering apparently is depleted) to lakes with somewhat lower pH and minimal buffering. The pH in the more sensitive lakes drops sooner and more rapidly, relative to the loading of SO_4^{2-}.

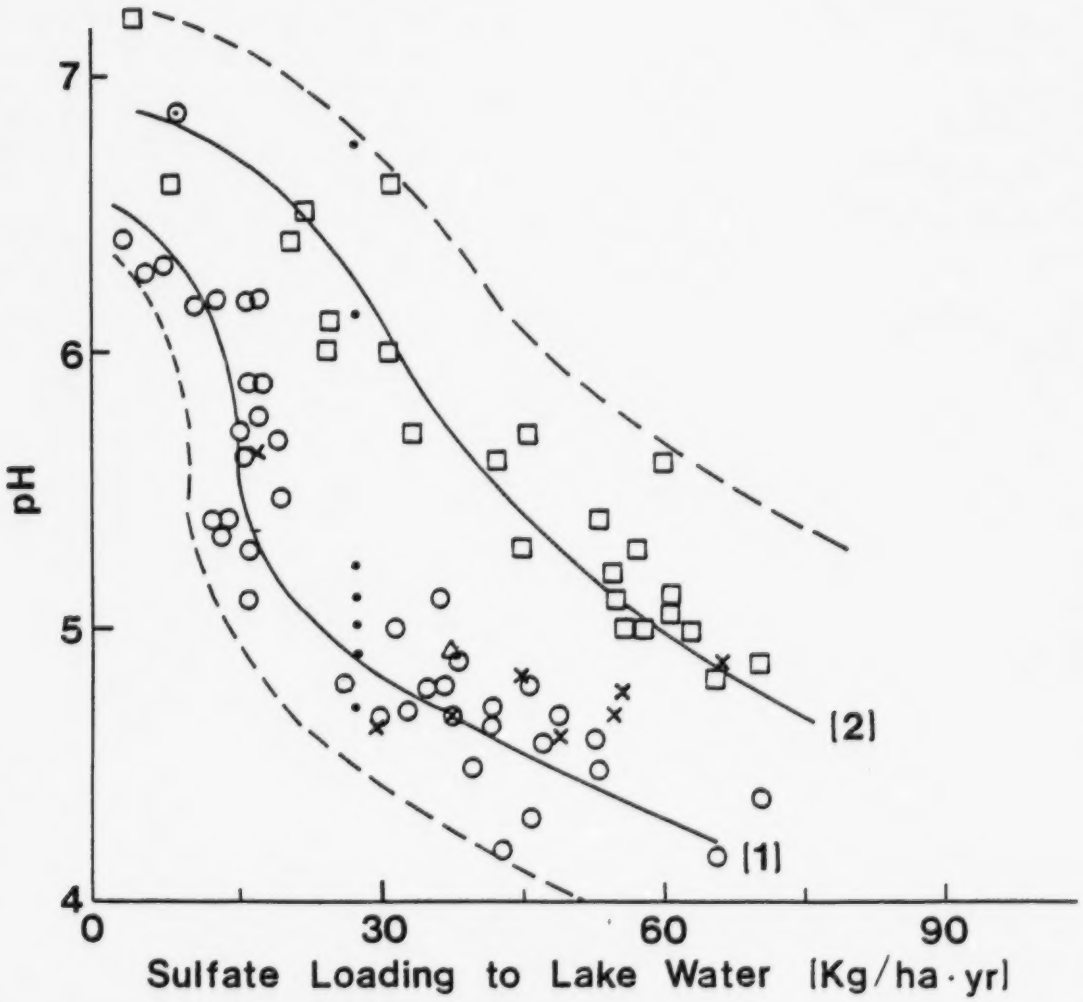

Figure IV-4. Effects of various sulfate loading rates on lake pH for lakes in very sensitive (1) and somewhat less sensitive (2) surroundings in Sweden. From Glass and Loucks 1980. Added points are for: · Florida (Crisman and Brezonik 1980); θ Como Creek (Lewis and Grant 1979); Δ Hubbard Brook (Likens et al. 1977); and X Norway (Wright and Snekvik 1978).

A graph of sulfate deposition versus lake pH could be used to express lake/watershed sensitivity, and therefore acid loading tolerance, by evaluating the position of the lake/watershed system on the response curves. For example, the lakes of southern Norway are underlain by granites and felsic gneisses (Wright and Snekvik 1978), and almost all prove to be somewhat sensitive. From a knowledge of the response of very sensitive geochemical/biological systems in moderately impacted systems, it appears possible to anticipate similar responses in the future on similarly sensitive systems if acidic inputs increase or are sustained.

Examination of Figure IV-4 suggests that annual sulfate loadings of less than 15 to 17 kg/ha would be unlikely to degrade lakes of the type represented in curve (1). However, if the lower envelope of the data distribution is viewed as a potential "family" of the most sensitive lakes and streams, these appear to be just barely free of potential acid loadings effects at an annual rate of 9 to 12 kg/ha·yr. Thus, two "tolerances" can be defined, one associated with a possible protection of nearly all sensitive aquatic resources, and the other with protection of something less than all sensitive lakes, e.g., only the half of the "sensitive" resources that lie above curve (1) in Figure IV-4.

Since these curves were developed on the basis of Swedish data, and represent a north-south geographic gradient in SO_4^{2-} loadings, and are not actual observations of acidification responses over time, these estimates of acid loading tolerances must be viewed very cautiously for application in a North American context.

The Henriksen Nomograph

Henriksen (1980) presents a model based on the concepts implicit in titration of a bicarbonate-buffered lake with strong acid (principally H_2SO_4) from the atmosphere. In the process, bicarbonate is depleted and lake pH can fall below 5 with consequent effects on aluminum mobilization and fish. These relations are basically the same as those in the Dickson work, and are summarized in the nomograph (Figure IV-5) using two key measurements:

(i) ambient concentrations of in-lake calcium (or Ca+Mg) as an estimator of the pre-acidification alkalinity; and

(ii) lake sulfate concentrations (in excess of marine input) as an estimator of H+ added to the system.

The resulting semi-predictive nomograph is divided into three sections:

(i) bicarbonate lakes, where original alkalinity was high and/or added H+ is low, so that the lakes remain bicarbonate buffered;

(ii) acid lakes, where original alkalinity was low relative to acid inputs, and all bicarbonate appears to have been depleted by the acid addition; and

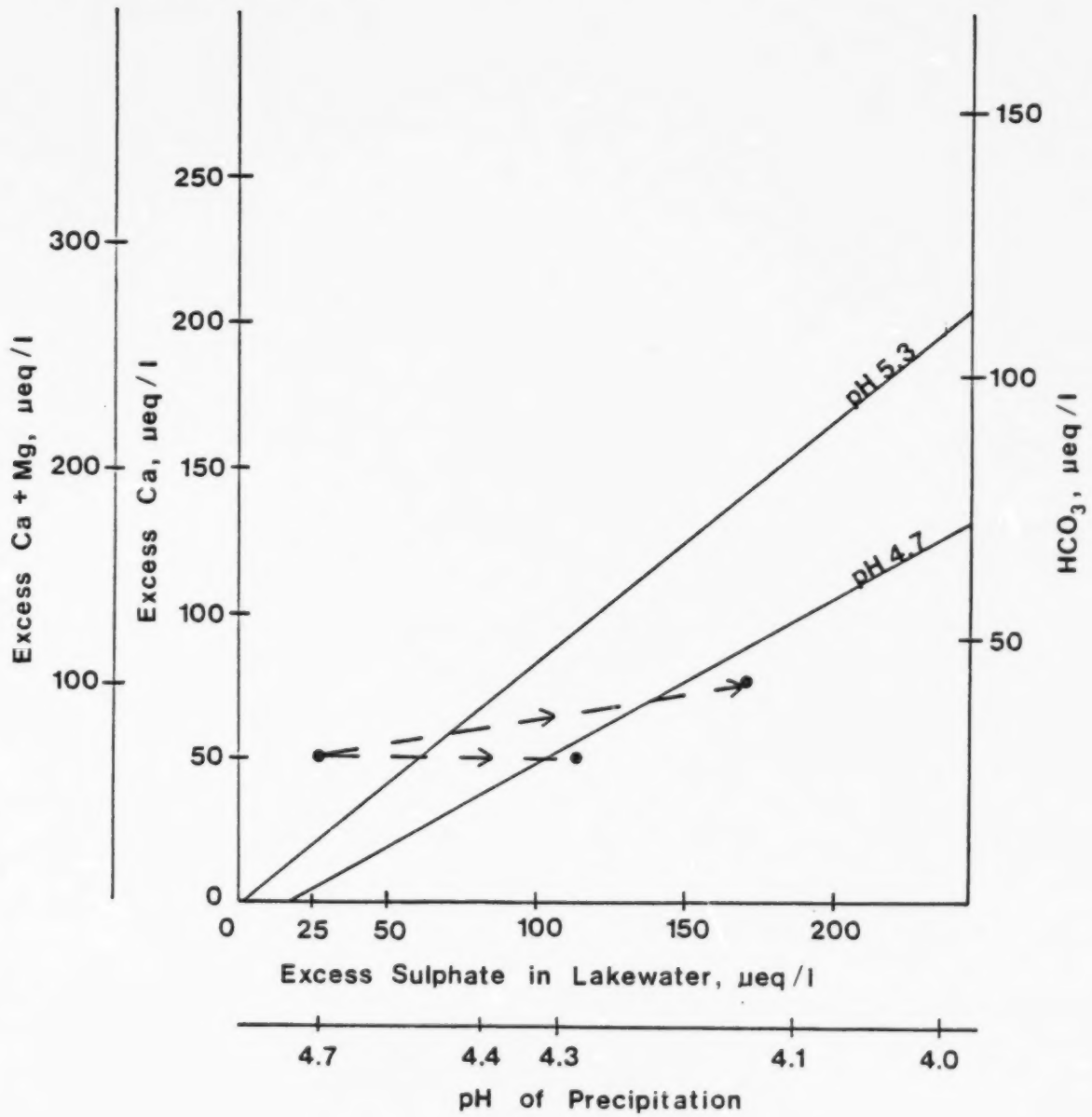

Figure IV-5. A nomograph to predict the pH of lakes given the sum of non-marine calcium and magnesium concentrations (or non-marine calcium concentration alone) and the non-marine sulfate concentration in lake water (or the weighted-average hydrogen ion concentration in precipitation). Nomograph also can be used to predict future changes in lake pH when precipitation acidity increases. (From Henriksen 1980.)

(iii) transition lakes, in which bicarbonate appears to be undergoing reduction (or is almost depleted) and large pH fluctuations occur during runoff events.

The transition phase, in which the lake is shifting from a bicarbonate-buffered equilibrium at moderate pH to an aluminum-buffered equilibrium at low pH, represents the key process requiring prediction. This shift apparently is forced by H^+ and SO_4^{2-} inputs, and Henriksen presents regression equations based on Norwegian lake and precipitation data for representing sulfate in lake water (SO_4^*) in terms of sulfate in precipitation [$SO_4(p)$] and H^+ in precipitation [$H^+(p)$]:

$$SO_4^* = -19 + 1.9\ SO_4(p)$$

$$SO_4(p) = -2.7 + 1.37\ H^+(p)$$

All concentrations are μeq/ℓ, and the sulfate is excess over that from marine origin. These equations have not yet been validated for North America.

The methodological component that can be applied to determine a threshold loadings tolerance must use assumptions as to the processes maintaining steady state lake pH in various types of aquatic resources, ranging from very sensitive to only moderately sensitive. Maintaining a pH of 5.3 would, presumably, prevent lakes from entering the "transition phase". This method, however, does not consider the depression of lake pH due to spring snowmelt, although the results (based on summer data) suggest the spring depression is being taken into consideration.

Episode Receptor Dose/Response Relation During Shock Events

A possible alternative model for describing and projecting aquatic resource response to acid loading emphasizes the non-equilibrium nature of the acidification process, equivalent to Henriksen's "transition phase". During this phase, aquatic ecosystems can show some buffering and a relatively unaltered pH during much of the year, but they also may experience sudden pH drops during hydrologic flushing events, i.e., at times when accumulated acidic material in the watershed is flushed relatively suddenly into streams and lakes. The rapid increases in H^+ concentrations can also mobilize Al^{3+} for a brief period, and the shock event can become a multi-agent toxic stress affecting the survival of fish and other organisms at various life stages, depending on the timing and magnitude of the pH depression.

Research on brook trout and Atlantic salmon by Daye (1980) and Daye and Garside (1975, 1976, 1977, 1980a, 1980b), and related research by Beamish (1974, 1976) and Harvey (1975, 1979, 1980a, 1980b) have provided a broad understanding of the response of several pH-sensitive fish species to both long-term and short-term elevated H^+ exposures. Mortalities of fish eggs, sac fry and adult fish have been viewed as a response to continuing chronic pH depression. At the same time, effects on egg viability, hatching success, and adult survival are known to occur as a response to short-interval acute H^+ and Al^{3+} exposures. The experimental data base supporting these relationships can be generalized to support the following statements (Andrews et al. 1980; see previous section).

(1) The short-term acute exposure, or shock effect, can be expected when pH drops by a range of 0.5 to 1.5 units of the pH scale in a background of pH 5.5. to 6.5; and

(2) These shock exposures may be significant at a pH above the level at which chronic effects ordinarily would be produced.

Taken together, these data suggest that for waters normally in a range of pH 5.5 to 6.5, a pH depression (Δ pH) of 0.5 to 1.0 can cause substantial, and physiologically significant, acid-induced alteration of water chemistry. This relatively large increase in H^+ during shock events may be occurring only in regions where acidic deposition already has produced a downward time-trend in stream pH and alkalinity, as shown in several monitoring programs. Data from very sensitive regions relatively free of long-term acid inputs (or in the first to second decade of moderate deposition) indicate it is unlikely that a short-term pH depression of these magnitudes can occur with an unusual watershed stimulus.

Given this dose/response relationship, a procedure for defining an acid-loading tolerance, or loading threshold, also can be suggested. The annual SO_4^{2-} loading which, when subjected to a defined flushing event (e.g., snowmelt or first major rainfall following drought), leads to the minimal biologically-significant short-term H^+ and Al^{3+} exposure, as determined by controlled environment studies.

The data available on pH depression during flushing events indicate a range in responses from very little to as much as 1.0 unit of the pH scale during snowmelt in northern Minnesota, a region of recent and only moderate acid deposition (Glass et al. 1981a). Depression of pH is shown to be in the order of 1.0 unit on the Shaver's Fork River in West Virginia (Dunshie 1979, Figure IV-6), to more than 2.0 units in the Adirondacks (Schofield 1980, Figure IV-7). Values in this range also have been reported for Hubbard Brook (Likens et al. 1977) and Plastic Lake, Ontario (Zimmerman and Harvey 1979). Jeffries et al. (1979) report spring pH depression in several Ontario lakes and streams of 0.3-1.2.

The data presently available on the general relationship between SO_4^{2-} deposition and pH depression (Δ pH) are presented in Figure IV-8. The dashed lines indicate areas of differing geological sensitivity (i.e., buffering capacity). It is also important to recognize that two types of streams will show little effect: "acidified" streams, those with pH in the range of 4.7 to 5.0 during much of the year, and which have gone through the "transition phase"; and well-buffered streams. Those likely to show appreciable pH depression are those believed to be experiencing the "transition phase" of Henriksen.

Pending further testing, a "significant" shock event response, defined as a Δ pH of 0.5 to 1.0 unit, may be a useful estimate of the annual SO_4^{2-} threshold loading required to produce an unacceptable level of pH depression (this level to be based on the controlled environment effects observed on fish populations). These estimates must be defined for watersheds within a specified sensitivity range, a limited range of hydrologic dilution (i.e., stream size), and with a defined return interval for the episode. Recurrence an average of once a year during critical life-

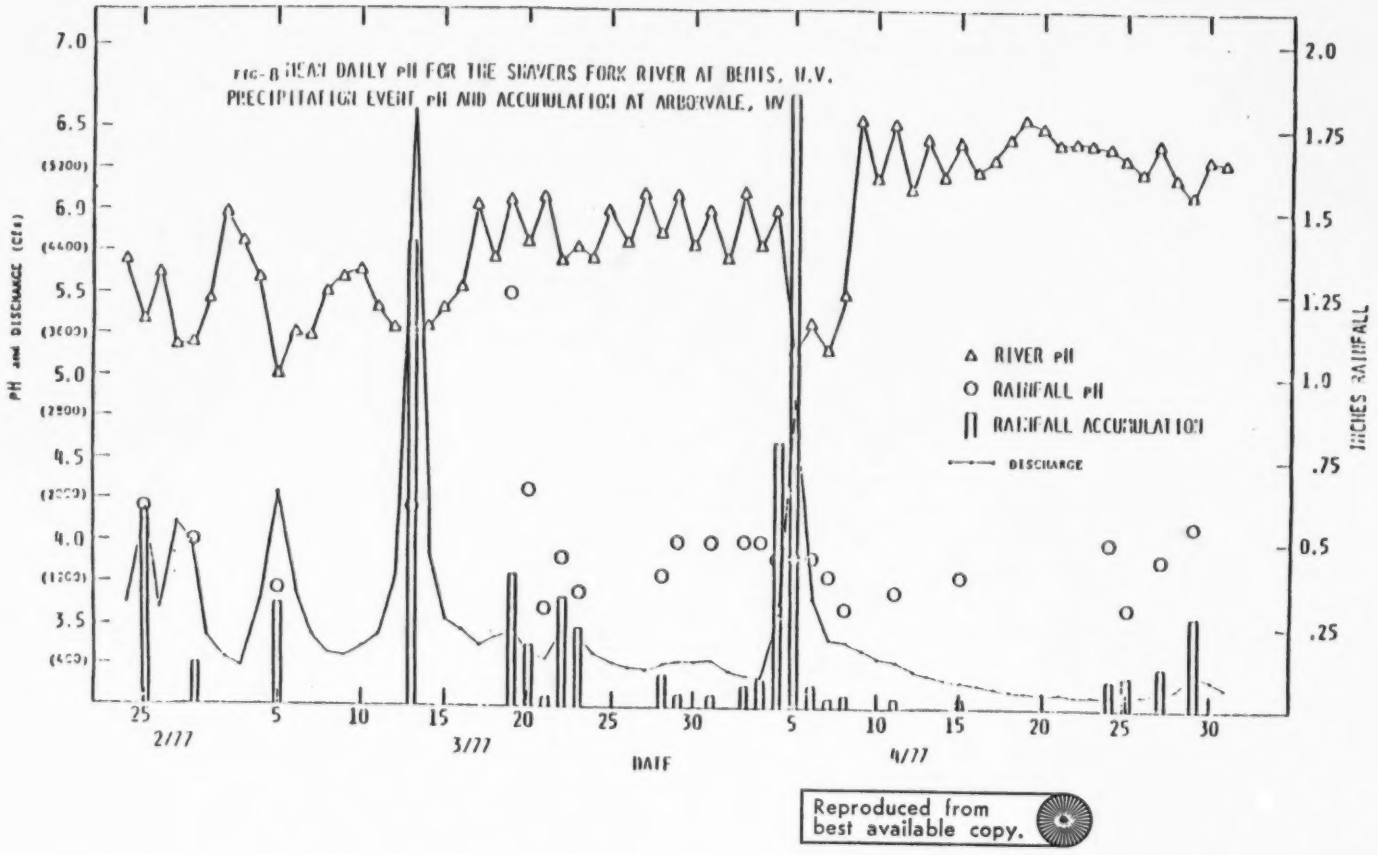

Figure IV-6. River pH, rainfall pH, rainfall accumulation and discharge rate for the Shavers Fork River, West Virginia, illustrating river pH depressions during snowmelt, when river acidity is generally greatest. Precipitation data were collected at Arborvale, West Virginia. (From Dunshie 1979.)

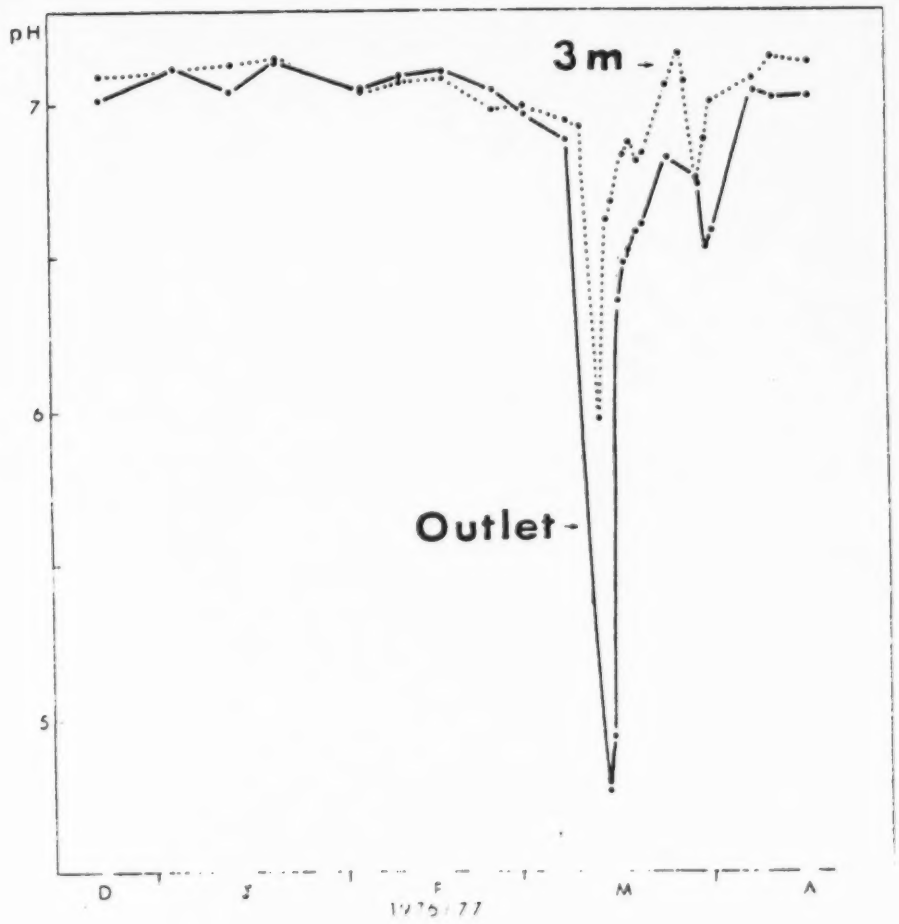

Figure IV-7. pH depression in Little Moose Lake, New York, occurring during spring snowmelt as measured in lake outlet and water entering the laboratory from a 3-m intake from the lake. Stream pH was more severely affected than lake pH. Little Moose Lake aluminum concentrations increased from pre-thaw levels of less than 20 μeq/ℓ to 320 μeq/ℓ during early thaw. (From Schofield 1980.)

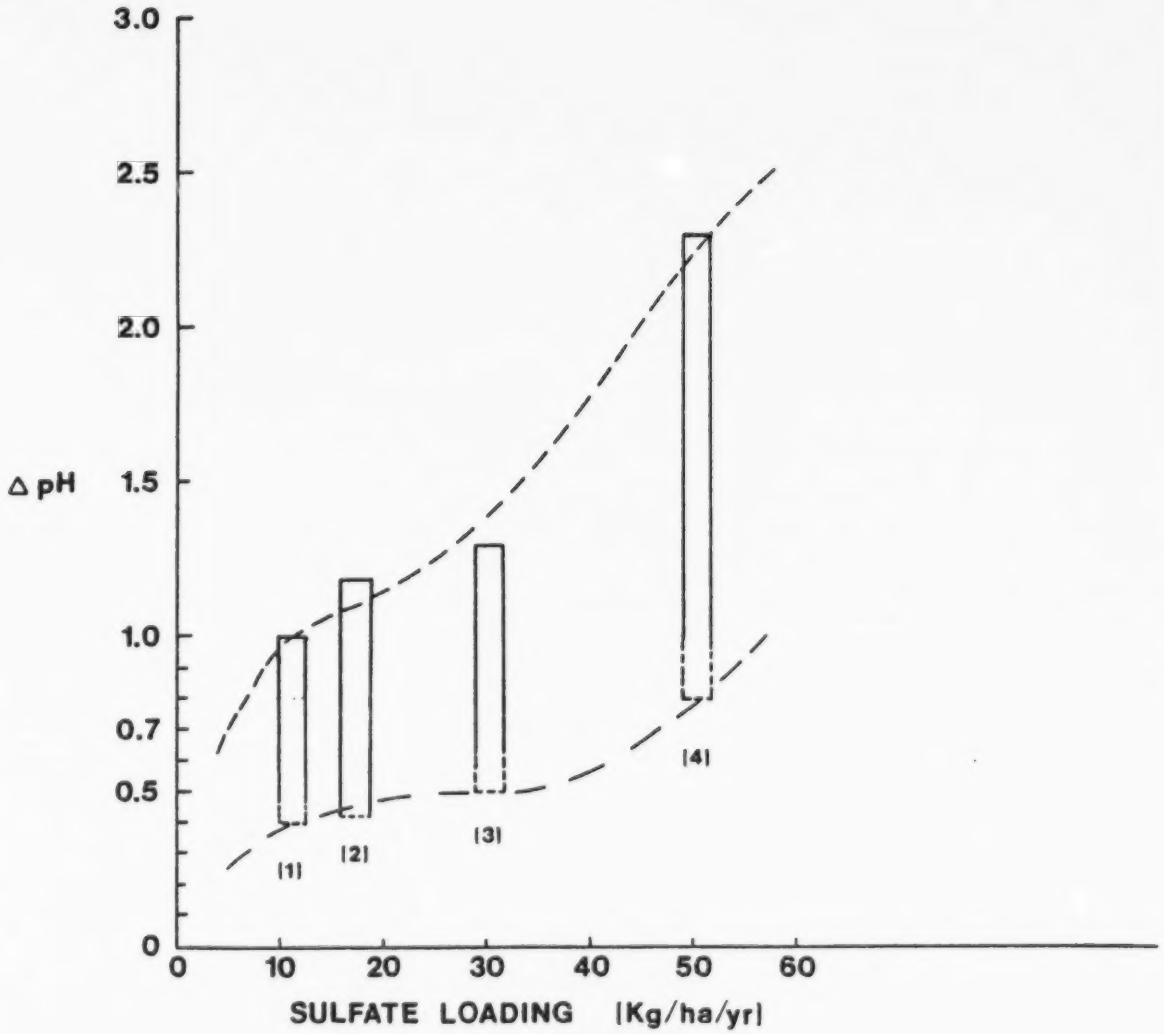

Figure IV-8. Relationship between sulfate loading rate and potential pH changes occurring during spring melt for sensitive areas (top dashed line) and slightly less sensitive areas (bottom dashed line). Rapid pH changes of 0.5 to 1.0 unit are considered detrimental to most fish species. Data shown are from: (1) Minnesota (Glass 1980); (2) Ontario (Harvey et al. 1981); (3) W. Virginia (Dunshie 1979); (4) New York (Schofield 1980).

cycle stages would be consistent with the physiological data base described above, and implicit in the model. Flushing events, however, appear to be possible at almost any time of the year and, therefore, could threaten other life stages and other species. From Figure IV-8, a sulfate loading of 5 to 7 kg/ha·yr is seen to produce a critical episode response (Δ pH) in the range of 0.5 to 1.0 for the most sensitive streams.

The major advantage of the above model is that it relates acid loading directly to biological effects of interest, namely, a pH depression sufficient to cause observable mortality of organisms at sensitive life stages. It also emphasizes non-equilibrium transition events, thereby predicting when resource impacts will tend to begin, not when they will be past and the lake or stream already acidified. The model also appears likely to apply equally to lakes as well as streams.

Although the episode receptor/dose relation incorporates physiological data on organism sensitivity to H+, further work is required to investigate fully the assumptions and relationships implicit in this approach to measuring water quality alteration and defining acid-loading tolerances. The model needs to be evaluated fully in relation to types of geological materials in the watershed, the past duration of acid loadings, the range in flow rates of the streams or seasonal rivulets, and the interval for deposition accumulation. It also needs to be evaluated for applicability in southern watersheds where snow does not accumulate and where flushing events are related to significant rainfall following drought (Dunshie 1979). Finally, the role for fish mortality of short periods of elevated aluminum concentrations must be investigated, particularly the apparent interactions with H+ (Schofield, personal communication).

SECTION V

RESEARCH AND DATA REQUIREMENTS FOR APPLICATION AND VALIDATION

This report has considered various measures of ecosystem alteration with respect to the effects of acid rain on terrestrial and aquatic ecosystems. The details of the measurement proposals, however, beg the question of what constitutes an appropriate or minimally sufficient description of ecosystem response. One should be particularly concerned that the "indicator" measures not be selected from a restrictive set that documents only a limited aspect of total ecosystem function. For example, concerns over eutrophication seldom take into account the larger changes in fauna and flora that accompany such processes--but more often restrict documentation to a few "water quality" parameters, reflecting the state-of-the-water chemistry.

Recognizing the need for a minimally sufficient set of well chosen measures to reflect the various dimensions of ecosystem transformation, Statistics Canada has developed a framework for environmental statistics which seeks to establish taxonomies, both for human stress factors and environmental responses, that are reflective of the major aspects of the environmental transformation process (Rapport and Friend 1979; Rapport and Regier 1980; Rapport 1981). With respect to ecosystem response, the provisional taxonomy for response measures includes indicators and integrators pertaining to the following ecosystem attributes: productivity, nutrient concentration and cycling, composition of the biota, quality of biota, and quality of the environment.

The measures discussed in this report cover a number of aspects of the overall response taxonomy. The forest site index reflects forest ecosystem productivity; the calcite saturation index deals with aspects of nutrient cycling; the toxicity measures refer to the quality of biota -- both with respect to mortality and morbidity; the composition of biota is best documented in the sequential decline in reproduction and ultimately extinction of various fish species in acidifying lakes. This latter work could be extended to identifying the more sensitive "functional groups" of species that are displaced as well as new groups of dominants that may become established. With respect to quality of biota, referred to above, measures of changes in size distributions (particularly stunting of trees), disease incidence on trees in acid-stressed areas, and failures to reproduce might also be included -- in addition to the toxic aspects already mentioned.

AN APPROACH TO ASSEMBLING SENSITIVITY MEASUREMENTS

A preliminary listing of the data needed to document lake and watershed sensitivity is given in Table V-1, effectively summarizing the various methodologies discussed previously. The table is meant only to suggest the range of factors involved in lake and watershed sensitivity, not to be comprehensive or complete at this time. However, one need not have all the listed data to estimate some of the integrative measures. A

TABLE V-1. LISTING OF DATA NEEDS AND COMPUTATION PROCEDURES FOR APPLYING SENSITIVITY MEASURES AND POLLUTANT LOADING TOLERANCE MODELS IN NORTHEASTERN NORTH AMERICA.

I. GENERAL WATERSHED DATA

Location:
Area (ha): Land _____ Water _____
% Urban _____ % Agricultural _____
% Forest _____ % Other _____

Mean Drainage Basin: Slope _____ Length _____
Water Flow Volumes: Input _____ Output _____
Water Flow Rates: Input _____ Output _____
Retention Time:
Avg. Precipitation (mm) _____ Mean Annual pH _____

II. GENERAL AIRSHED DATA

Regional Atmospheric Bulk Loading (kg/ha·yr): SO_2 _____ NO_x _____
SO_4^{2-} _____ NH_4^+ _____ Pb _____ Hg _____ Cd _____
Regional Cumulative Growing Season Exposure ($\mu g/m^3 \cdot yr$ above background): O_3 _____

III. SOIL SENSITIVITY DATA

Major Soil Types _____ Parent material _____

	O_2	A_1	A_2	B_1	B_2
Horizon Depth (cm)					
CEC (meq/100g)					
Base Saturation (%)					
Soil pH (water)					
Soil texture					
Extractable ($\mu g/\ell$) Al					

Soil Sensitivity: Non-sensitive Slightly sensitive Sensitive
McFee _____ _____ _____
Coote et al. _____ _____ _____

IV. FOREST SITE INDEX SENSITIVITY DATA

Major Plant Communities: _____
Dominant/Codominant Tree spp. _____
Age of Dominants _____
Height of Dominants _____
Understory Spp. _____
Field Measurement of SI (ft.) _____
Regression Estimate of SI (ft.) _____
Calculated Nutrient Loss (Gain) Due to Acid Deposition (kg/ha·yr):
Ca _____ Mg _____ K _____ Other _____
Calculated peak AL^{3+} ($\mu g/\ell$) _____
Estimated SI with Nutrient Change and Al^{3+} (ft.) _____
Estimated Change in Annual Fiber Production (kg/ha) _____

TABLE V-1. (continued)

IV. AQUATIC SENSITIVITY DATA

pH _____ Alkalinity (meg/ℓ) _____
Specific Conductance (μmhos/cm) _____
Secchi Disk Transparence (m) _____
Concentrations (mg/ℓ): DOC _____ POC _____ Ca^{2+} _____ Mg^{2+} _____
$K+$ _____ Na^{+} _____ NO_3- _____ NH_4+ _____ SO_4^{2-} _____
PO_4^{3-} _____ HCO_3- _____ Al _____ Mn _____ Fe _____
ZN _____ Cu _____ Hg _____ Cd _____

Calcite Saturation Index

$$CSI = p(Ca^{2+}) + p(Alk) - p(H+) + 2$$

1. Ca^{2+} (mol/ℓ) _____; p (Ca^{2+}) _____
2. Alk (eq/ℓ) _____; p (Alk) _____
3. $H+$ (eq/ℓ) _____; p ($H+$) _____
4. CSI = _____

(<1 . . Non-sensitive; 1-3 . . Potentially Sensitive; >3 . . Sensitive)

Henriksen Nomograph (See Figure IV-5)

1. Ca^{2+} conc. _____ (μeq/ℓ)
2. Mg^{2+} conc. _____ (μeq/ℓ)
3. Excess SO_4^{2-} _____ (μeq/ℓ)
4. Lake Status: Acidified _____
   Transition _____
   Bicarbonate _____

(Based on Henrikson, 1980)

Dickson Relation

SO_4^{2-} loading (kg/ha·yr) _____
Lake pH _____
Sensitivity category (see Figure IV-4) _____

V. FISH SENSITIVITY DATA

Chronic effects: Al (mg/ℓ) _____ pH _____
(See Tables III-3 and III-4)

Shock effects: SO_4^{2-} loading _____
Sensitivity category (from Dickson) _____
Predicted Δ pH _____
Predicted peak Al _____

viable sensitivity assessment strategy would fill in these data needs as studies or existing resource surveys (e.g., soils are assembled for assessment purposes).

- General Watershed Data

Coarse estimates of lake/watershed sensitivity could be made through evaluation of the data collected under this heading. For instance, a watershed with a large percentage of urban and agricultural land (and associated fine particulate runoff) is unlikely to be as sensitive as an area with a large proportion of forest and water. Knowledge of water flow rates, volumes and soil retention time also is important in assessing the ability of soils to neutralize acidic inputs.

- General Airshed Data

Application of the Site Index measure requires the use of several dose/response relationships for sensitive tree species. Thus, ozone and other gaseous pollutants should be available from regional monitoring. In addition, use of Almer/Dickson relation, Henriksen Nomograph and pH shock effects models requires measuring the atmospheric loading of acidifying substances.

- Soil Sensitivity Data

The data needs listed here are derived from McFee (1980) and Coote et al. (1980). Extractable aluminum should be measured to allow preliminary estimation of potential toxicity problems, should sulfates accumulation in soils reach that point. Together, these data provide a broad-scale assessment of sensitivity.

- Site Index Sensitivity Data

Forest site index is proposed as an integrative measure for terrestrial sensitivity because oxidants, aluminum toxicity and nutrient losses can all affect the rate of height growth, a term that translates readily into terrestrial productivity. The magnitude of site index decreases, therefore, represents a measure of the resulting loss in wood fibre production due to O_3 and acid deposition.

- Aquatic Sensitivity Data

The methodologies for evaluating aquatic sensitivity have been developed to a greater extent than terrestrial methodologies, but field validation is still required. The data needs listed here are based on the methodologies of Kramer (1976), Henriksen (1980) and Almer et al. (1978), as discussed in previous sections. Monitoring heavy-metal concentrations would help to define potential toxicity problems.

- Fish Sensitivity Data and Watershed Tolerance

The chronic effects of pH and aluminum on fish reproduction have been described as fully as possible, although more work on aluminum toxicity will be important. The pH and aluminum shock effect on various life-

stages of fish is a dose/response relationship now being developed and in need of validation. Development of this methodology is critical, as it is the only measure that bears directly on the biological effects of acid precipitation.

OTHER INFORMATION/RESEARCH NEEDS FOR SENSITIVITY MEASURE VALIDATION

A considerable amount of research will be necessary to show that the measures given above are adequate and appropriate to determining forest, lake/watershed sensitivity. While a variety of data needs is implicit throughout the previous discussion, this section attempts to summarize necessary research according to major subject areas.

- Effects on Forest Productivity

Since forest site index is a highly integrative measure, it reflects a variety of effects mechanisms, including oxidant damage to foliage, nutrient addition and depletion, and the toxic effects of H+, aluminum and heavy metals. The magnitude of the effect on height growth in relation to the combined dose must ultimately be measured in the field, not simply calculated from a variety of separate studies. In general, much more data are needed on the response of various forest species and entire communities to the various toxic agents.

- Sulfate and H+ Transport

The movement of H+ within the sytem is, along with movement of the anion (SO_4^{2-}), fundamental to predicting all other effects. Water flow patterns influence the pathways of SO_4^{2-} and H+ transport and the interaction with other system components. Simple quantitative methods are necessary to predict water flow patterns in relation to soil type, topography, rate of flow and other relevant variables. Of particular importance is study of flushing event processes as they affect SO_4^{2-} and H+ contact with the soil, and the regulation of the nitrogen and sulfur cycles in soil. The theoretical considerations of these questions given in this paper need to be supplemented with experimental work and watershed mass balance studies.

- Nutrient Cation Stripping

While theory and some field studies indicate acid precipitation leads to leaching of cations such as calcium and magnesium, other field studies indicate such losses may be small. Quantitative studies of nutrient stripping and the consequential effects on forest productivity are needed, therefore, for a variety of soils with different rates of acidic inputs. This is especially important in soils which are not now acid, but have relatively low base saturation.

- Aluminum Mobilization

The relationship between SO_4^{2-} and H+ input to a watershed and the subsequent output of soluble aluminum must be studied on the watershed as well as the soil column level. Of critical importance are the effects of

variation in slopes, soil type and water flow (flushing event) patterns. In order to predict the occurrence of spring or fall aluminum flushes, one must understand the dynamics of water flow during snowmelt or other flushing events as water penetrates various soil horizons. Research requirements include comparative watershed studies as well as regionally placed lysimeter studies.

- Role of Organic Substances in Water

Superimposed on many of the H+ and metal mobilization processes and effects are the modifying influences of organic molecules within the system. These range from buffering of H+ input, to detoxification of aluminum, to mobilization and transport in chelated form of various elements and compounds. At the present time, many of these processes are poorly understood, particularly in aqueous media. Further research should identify sources of organics in a variety of soils and determine quantitatively the impact of the amounts and kinds of organics being observed.

- Other Aquatic Effects

Most of the questions concerning aquatic effects center around the dose/response relationships of H+, aluminum and heavy metals for fish and other components of the aquatic community. Of particular concern are potential synergisms between the various toxicants and overall community and ecosystem responses. Effects on fish-eating birds and mammals as a lake/stream fishery declines, and certain species are eliminated, must be investigated fully. It is possible that research in this area may identify additional broadly based measures of aquatic ecosystem stress comparable to the site index for forests.

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